Cohen

ADOLPH STRECKER'S

ORGANIC CHEMISTRY.

ADOLPH STRECKER'S

SHORT TEXT-BOOK

OF

ORGANIC CHEMISTRY.

BY

DR. JOHANNES WISLICENUS,
PROFESSOR OF CHEMISTRY IN THE UNIVERSITY OF WÜRZBURG.

TRANSLATED AND EDITED, WITH EXTENSIVE ADDITIONS, BY

W. H. HODGKINSON, PH. D., AND A. J. GREENAWAY, F. I. C.

NEW YORK:
D. APPLETON AND COMPANY,
1, 3, AND 5 BOND STREET.
1882.

PREFACE

TO

THE ENGLISH EDITION.

THE great popularity which Professor Wislicenus's edition of Strecker's 'Text-book of Organic Chemistry' has enjoyed in Germany leads to the belief that an English translation will be acceptable. In the interval that has elapsed since the publication of this book in Germany considerable additions have been made to our stock of knowledge in organic chemistry, necessitating many alterations and additions to the text. On this subject Professor Wislicenus has written as follows:—

'I willingly give permission to publish a translation of my work, and only beg that regard shall be had—so far as the scope and purpose of the book necessitate—to the largely increased material and essentially nearer insight into the relations and nature of the organic compounds already known that has been obtained since the publishing of my book. So far as this is done it will be the work alone of the translators, as, from the occupation of my time by official duties, I have found it impossible to take part in the very necessary corrections and additions.'

From this it will be seen that the translators are entirely responsible for such alterations as have been made, these being most numerous in the part on the aromatic compounds. In the case of the naphthalene compounds it has been thought advisable to introduce the symbols proposed by Reverdin and Nölting as the most suitable provisional notation.

In conclusion the translators have to express their thanks to Mr. R. Meldola for the account of the diazo colours that has been printed as an appendix.

LONDON:
June 1881.

compounds and their constant employment in the synthesis of organic substances; with the cyanogen group are almost necessarily included the carbon oxyamides and guanidine.

The most systematic arrangement would be founded on the number of carbon atoms in direct union. In each such group of equal carbon contents the paraffin would come first, next those derivatives in which only a single hydrogen atom had been replaced, these being further arranged according to the valency of the substituting element. Then would follow the di-substitution products, i.e. the derivatives of the hydrocarbon nucleus C_nH_{2n}, arranged according to the relative order of the two positions of replacement. Next would follow the trisubstituted paraffins—compounds of the nucleus C_nH_{2n-1}, &c., arranged according to analogous principles. Erlenmeyer has commenced this classification in his text-book, unfortunately as yet without passing beyond the dicarbonides.

This order of arrangement is very valuable for the study of organic chemistry, more so, however, for those moderately well acquainted with the subject than for beginners. For the latter, I do not consider the study of homologous series to be superfluous, especially in the early part of a text-book. In this way alone can the clear differentiation of the various categories of bodies be made evident, depending as they do not so much on the accumulation of carbon atoms as on the nature and amount of the other elements in union. In addition to this the study of these series considerably assists the perception and mastering of the substance of the book and the grouping of large numbers of facts under typical reactions. In this form we can advance the otherwise over-worked theory of types into a wider field. In every homologous series there can, then, be made out the laws of evolution and complication with increasing number of carbon atoms as well as the order of structural synthesis.

As far as the selection of the facts to be considered is concerned, I follow in general those principles which have hitherto characterised Strecker's text-book. That additions are required by the chemical results of the last few years is self-evident. The simpler categories of chemical compounds, such as the derivatives of the alcohol radicals C_nH_{2n+1} and the next more complex group, required broader treatment in many places, whilst the compounds of the nuclei poorer in hydrogen could be treated more shortly, as those relationships already mentioned would otherwise be repeated.

The group of benzene derivatives has, as is generally customary, been considered separately. The time is probably not far distant when such a separation will be neither necessary nor advisable; it will not, however, come until the gaps still existing between the aromatic and fatty groups have been filled up, and further proof given of that continuity of group relations which is already visible.

In the present state of our science we cannot neglect the frequent use of structural formulæ based on the valency of the chemical elements. Their partial uncertainty and in many points tangible shortcomings need not prevent their use to some extent in a text-book, although their use requires care. With regard to the manner of writing the constitutional formula, no dogmatic adherence to any single method will be adopted, so that the formula of one and the same substance may be found varyingly written in different places. With every one of these systems of formulæ there is the danger of substituting a concrete image in place of an idea. These images we certainly cannot do without, but we must keep the idea lying behind such an image as far as possible pure, and also mobile, seeing that in comparison with older views we have in it only relative, not absolute truth.

I hope that this text-book in its new form may be found to have sufficient merit to justify its existence, that its imperfections may not impede its usefulness to either scholar or teacher, and that it may in the future maintain that rank which it had acquired under Adolph Strecker's care.

JOHANNES WISLICENUS.

WÜRZBURG.

CONTENTS.

APPENDIX.

ORGANIC CHEMISTRY.

INTRODUCTION.

1. UNTIL the early part of the present century organic chemistry was defined as the study of those bodies derived from the working of animal or vegetable life, together with their numerous compounds and derivatives. It was assumed that for the conversion of mineral substances into organic bodies there was requisite a peculiar force only existing in the living organism, and essentially different from that which regulated the apparently simpler laws of mineral chemistry.

The enormous development of organic chemistry in recent times has, however, gradually obliterated this line of distinction between organic and mineral bodies.

The number of organic bodies built up from their elements, or from their simplest mineral combinations, is on the increase, and the results in the region of artificial synthesis approximate nearer and nearer to the highest stages of chemical complication—the immediate agents of organic life—the cellular constituents of plants and animals.

The laws which govern organic synthesis have shown themselves to be in no way different from those concerned in the changes and combinations of mineral substances.

The best arbitrary definition of organic chemistry is one depending on the fact that all organic bodies contain carbon as the essential constituent, for it is to the chemical characteristics of carbon alone that the compounds termed organic, compared with mineral compounds, owe their peculiar character.

2. *Constituents of Organic Bodies.*—Naturally occurring organic bodies contain but a limited number of elements in combination with carbon, many only hydrogen or oxygen; many more contain both hydrogen and oxygen, and others again, these in addition to nitrogen, sulphur or metals.

By artificial methods all the elements may be obtained as integral constituents of carbon compounds, the base forming metals giving salts with organic acids being in this way combined to the carbon by means of oxygen, sulphur, &c., and also many elements combining directly to the carbon, in most of which cases the elements lose their distinctive characters, by which they are known in mineral or inorganic compounds, and are only discoverable after the action of the most powerful reagents or the employment of a high temperature, by which all organic compounds are more or less decomposed or destroyed.

3. The determination of the composition of an organic body is a primary step towards an exact knowledge of its nature and constitution, and the chemistry of the carbon compounds received a great impetus from the discovery of exact methods of organic elementary analysis.

Before proceeding to the determination of the proportions, by weight, of an element contained in a compound, all the other elements or constituents of the body must be known, since methods of analysis must be varied according to their nature and peculiarities. Qualitative analysis must therefore always precede quantitative. In naturally occurring bodies it is necessary to test for the presence of carbon, hydrogen, oxygen, nitrogen, sulphur, and the constituents of the ash or residue left on combustion. In artificial bodies built up from their elements this is not necessary, as the individual components are already known.

In the following sections an outline of the general methods employed will be given.

QUALITATIVE ELEMENTARY ANALYSIS.

4. *Carbon.*—Most organic bodies, on heating out of contact with air, decompose with blackening from separation of carbon. Volatile bodies are passed through hot tubes, on which they give a black deposit. It is better to depend on the formation of carbonic anhydride when the body is burnt with oxygen, a test of universal application. For this purpose non-volatile bodies are mixed with cupric oxide and heated; volatile bodies or gases are led over ignited cupric oxide; the carbonic anhydride formed is then passed into a solution of calcic hydrate, with which it gives a white precipitate of calcic carbonate.

5. *Hydrogen.*—The presence of hydrogen is shown by heating the dried substance with cupric oxide, when water is formed, which collects in drops on the cold portions of the apparatus. Organic bodies containing oxygen as well as hydrogen give off water when heated alone.

6. *Nitrogen.*—Most nitrogenous bodies, when heated alone in a glass tube, give an odour of burnt feathers, whilst ammonia is evolved, and can be recognised in the vapours by its turning red litmus paper blue. In many cases volatile acids are evolved at the same time, which completely neutralise the ammonia. It is better, therefore, before ignition, to mix the body under examination with an alkaline hydrate; soda lime is generally employed. This latter, at high temperatures, directly oxidises the organic body, completely retains the carbonic anhydride formed, whilst the nitrogen, uniting with the hydrogen of the organic substance or of the alkaline hydrate, is evolved as ammonia.

Very small quantities of nitrogen are, however, readily overlooked by this method, which also frequently fails if the nitrogen is united to oxygen, as nitryl (NO_2), in the organic body. The following method is of general application and completely certain :—A small quantity of the substance is mixed with a little sodium or potassium (with addition of dry sodic carbonate in the case of explosive substances) and heated in a test tube; the action is generally accompanied by a slight explosion. The residue is boiled with water and some ferrous sulphate, and then acidulated with sulphuric acid; a ferrocyanide is thus obtained, which, on addition of a drop of ferric salt, gives a precipitate of Prussian blue.

7. *Sulphur and Phosphorus.*—These and other analogous acid-forming elements (such as selenium, tellurium, arsenic, antimony) are most conveniently tested for by heating the suspected body with a mixture of pure potassic carbonate and nitrate. The aqueous solution of the white fused mass is then tested in the usual manner for sulphate, phosphate, &c.

8. *Halogens.*—In those cases where the aqueous solution of the substance gives no indication, a small quantity of the body is heated with pure lime in a test tube. The residue is dissolved in dilute nitric acid, and a few drops of argentic nitrate added; a white curdy precipitate indicates chloride, bromide, or iodide. The separation of these elements is conducted in the usual manner.

9. The examination for other elements is, as a rule, made by ignition of the organic substance and examination of the ash. Only very volatile metals are overlooked without further precautions. Mercury compounds, e.g., are ignited in a glass tube in a current of oxygen, the liquid metal then condensing on the cold portion of the tube.

It is not generally practicable to prove the presence of oxygen directly, the complete quantitative analysis alone showing its presence without doubt.

QUANTITATIVE ELEMENTARY ANALYSIS.

Estimation of Carbon and Hydrogen.

10. Carbon and hydrogen are estimated in a single operation. A weighed quantity of the substance is burnt, converting the carbon into carbonic anhydride and the hydrogen into water; these latter are then conveyed into weighed absorption apparatus, and the carbon and hydrogen calculated from the increase of weight observed.

Pure cupric oxide is the material usually employed in the combustion; at a red heat it readily gives up its oxygen to the organic bodies, being thereby reduced to metallic copper. The water is absorbed in glass tubes (fig. 1) containing either porous ignited calcic chloride or fragments of pumice stone saturated with concentrated sulphuric acid. The greater part of the water condenses in the liquid state in the small bulb above the bend of the U tube, the non-condensed vapour being absorbed in its passage through both limbs of the apparatus. The carbonic anhydride is absorbed by strong solution of potassic hydrate (sp. gr. 1·27), contained in Liebig's potash bulbs (fig. 2). In these the gas first passes into the largest bulb, from which it expels the potassic hydrate, and then passes in single bubbles through the other bulbs, and being thus necessarily in long contact with the potash, is very completely absorbed. The modification of this apparatus known as Geissler's bulbs is also much used. Instead of potash solution, soda lime is frequently used to absorb carbonic anhydride. This is rubbed in a porcelain mortar until a mixture of fine powder with pieces the size of coarse millet remains. U-shaped light glass tubes (fig. 3), which contain in one limb, between two plugs of cotton wool *a* and *b*, coarsely powdered calcic chloride, are completely filled up with the soda lime; by tapping the tube with both limbs placed horizontally the separation of the fine from the coarse powder is effected. The latter occupies the upper part of the cross-section, and forms a passage through which the gases pass, and from which the finer powder absorbs the carbonic anhydride. In cases where soda lime tubes are employed a small bulb tube *g*, containing a drop of sulphuric acid, is usually placed between the calcic chloride and soda lime tubes; it serves to show the rate at which the combustion is progressing.

Fig. 1.

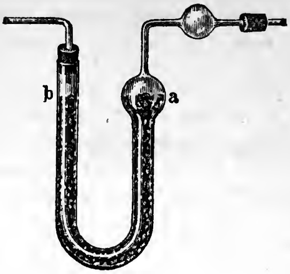


Fig. 2.

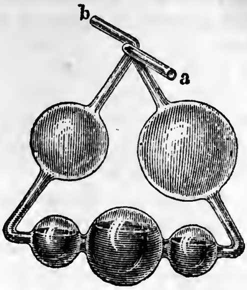
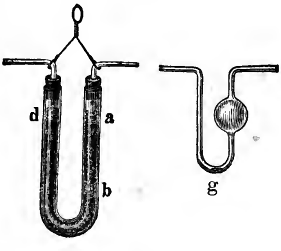


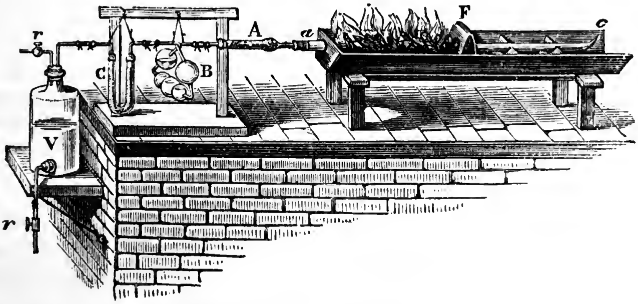
Fig. 3.



Combustions are conducted in many different ways. Two methods will be described, of which the oldest and, as regards apparatus, the simplest will always be connected with the name of Liebig. The solid substance to be analysed, having been dried and previously finely powdered, is weighed (generally 0·2 to 0·3 gram is taken) and mixed with finely powdered cupric oxide in a warm porcelain mortar. The cupric oxide must have been ignited just before the operation, transferred whilst still hot to a wide glass tube, which is then carefully closed, and cooled so far as not to alter the organic substance when mixed with it. A tube of difficultly fusible glass must have been previously prepared for the reception of the mixture. This *combustion tube* (fig. 4) is drawn out at one end (over the blowpipe) to a tail at an obtuse angle, then carefully cleaned and dried. The end is filled up to *c* with pure cupric oxide; then follows the mixture of the organic substance and cupric oxide to *b*; from there to *a* is the cupric oxide used in rinsing out the mortar. The tube is then filled up to within an inch of its mouth with pure cupric oxide, and finally a loose plug of asbestos is inserted. The length of the layer of cupric oxide must vary with the combustibility or volatility of the organic body, so that for such bodies as give on heating a large volume of combustible vapours and gases it must be made longer than it otherwise would. The tube is then held horizontally and tapped gently, by which means a canal is formed along the top of the contents, along which the products of combustion can pass. The tube so prepared is then laid in a combustion furnace; the chloride of calcium tube is fitted on by means of a good cork or caoutchouc plug, and in its turn is connected to the potash bulbs by means of a piece of caoutchouc tubing. The whole apparatus is shown in fig. 5. The fore-part of the combustion tube is now heated, and as soon as the cupric oxide is glowing the heating gradually carried backward, so that the mixture of substance and cupric oxide is raised to the temperature necessary for combustion.

FIG. 4.

FIG. 5.



In order to prevent any condensation of unburnt volatile decomposition products in the tail, that is kept heated from the boundary of the pure cupric oxide. When, at length, the whole tube is brought to a red heat, and no more gas bubbles are seen in the potash bulbs, the combustion is finished. The tail of the combustion tube is broken off at *c* and air drawn slowly through, so as to sweep all products of combustion from the tube into the absorption apparatus. At the finish the apparatus is disconnected and the absorption tubes weighed. As carbonic anhydride contains $\frac{3}{11}$ of its weight of carbon, and water $\frac{1}{9}$ of its weight of hydrogen, by multiplying the increase in weight of the respective tubes by these figures, the amount of carbon and hydrogen in the substance employed will be obtained.

11. When readily volatile liquids have to be analysed in this apparatus they are placed in small previously weighed bulbs, the point fused, and the bulb again weighed, in order to ascertain the weight of the substance taken. The combustion tube is then filled for a quarter of its length with freshly ignited cupric oxide, the bulb, with its point broken, then dropped in, and the tube filled up with cupric oxide. The apparatus is arranged as in fig. 5; the front and back parts of the tube first brought to redness, and then that part where the bulb is gradually heated, so that the vapour of the liquid shall slowly pass over the glowing oxide and be completely burnt.

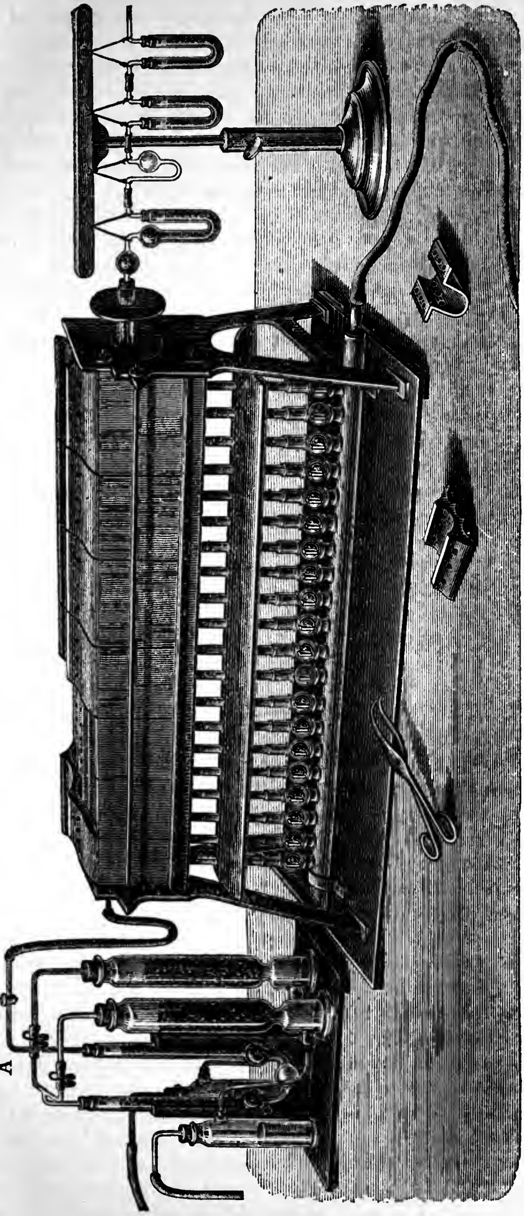
Non-volatile liquids, fats, &c., are caused to spread over the sides of the combustion tube, which is then filled up with cupric oxide.

12. In many cases it is necessary to make some alterations in the method above described. Some organic substances cannot be completely burnt with cupric oxide, either from not admitting of sufficiently intimate admixture or from their yielding much carbon on heating, which cannot come into contact with sufficient cupric oxide for its complete combustion. In these cases plumbic chromate is employed instead of cupric oxide. Immediately before use it must be strongly heated in a porcelain basin. It contains more oxygen in an equal volume than cupric oxide, fuses on heating, and gives off oxygen on strong ignition. Plumbic chromate is of use also in the analysis of bodies containing sulphur and halogens, as it completely retains them; whilst with cupric oxide sulphurous anhydride or free halogen is frequently obtained, which being soluble in potassic hydrate, would completely spoil the result for carbon. Nitrogenous bodies on combustion frequently give off a portion of their nitrogen as nitric oxide, which, when mixed with air, is absorbed by potash, and would also bring the result too high. In this case a layer of a mixture of potassic chromate and manganic oxide is placed in the front part of the combustion tube, and kept very gently heated during the combustion, whereby all nitrous fuses are effectually removed.

FIG. 6.

13. Much saving of time, together with simplification of manipulation and greater certainty in the results of carbon and hydrogen estimation, is obtained by combustion in a stream of oxygen in a tube open at both ends (fig. 6). Between the asbestos plugs *d* and *e* a layer of granulated cupric oxide is placed; the ends of the tube are closed by bored corks, in one of which is placed a tube for the introduction of pure air or oxygen, whilst the other serves to connect with the absorption apparatus. The combustion tube is heated to redness in the furnace, whilst a stream of dry air is passed through; by this means the whole apparatus and its contents are obtained thoroughly dry and ready for immediate use. The absorption tubes for water and carbonic anhydride having been attached, the weighed substance contained in a porcelain or platinum boat *c* is pushed in (volatile liquids

Fig. 7.



in bulbs as described), and finally a short glass rod with fused edges *l*, which nearly fills the tube. The object of this latter is to cause an acceleration of the gas stream at that point, and so prevent any chance of the vapours given off by the burning body travelling backwards, as they might otherwise do, the stream of gas being necessarily slow, to ensure complete combustion. The whole apparatus shown in fig. 7 being arranged, and the substance in its boat placed behind the red-hot cupric oxide, heat is next applied at the place where the glass rod is (*b*, fig. 6) and then slowly advanced to the boat. At the commencement purified air may be employed, the oxidation being mainly effected at the expense of the cupric oxide; later oxygen is turned on from a second gas-holder, and the complete oxidation of any carbon left behind is then effected; any reduced copper is also re-oxidised. Both air and oxygen are purified by passing through potash and calcic chloride or sulphuric acid. The stream of oxygen is continued until its presence can be distinctly observed at the absorption apparatus; it is then displaced by a current of air. The cooled absorption tubes and the boat, if any ash is left, are then weighed. The combustion tube can then be employed for a fresh analysis, as it is in a state of complete readiness, i.e. completely free from water and carbonic anhydride and charged with pure cupric oxide. In the case of nitrogenous bodies potassic chromate and manganic dioxide are placed in the anterior portion of the tube. With substances containing halogens a roll of silver must be placed in front of the cupric oxide; by this every trace of halogen is absorbed. Bodies containing sulphur must be burnt with plumbic chromate, or if cupric oxide and oxygen be used the gas stream must be passed over pure plumbic peroxide, heated to but little above 100°, by which all sulphurous anhydride is removed.

Estimation of Nitrogen.

14. The determination of the amount of nitrogen in organic bodies is effected either by measuring the nitrogen in the free state and calculating the weight from the volume, or by conversion into ammonia.

The first method can be applied to all organic bodies; the second does not give satisfactory results in those cases where the nitrogen is in union with the oxygen of the organic substance (e.g. in nitro compounds).

15. *Estimation of Nitrogen by Volume.*—By the combustion of nitrogenous organic bodies with cupric oxide there results, as already mentioned, carbonic anhydride, water, and nitrogen, and probably some quantity of nitric oxide, this latter being reduced to nitrogen by passing over red-hot metallic copper. On cooling the products of combustion, the water is separated in the liquid form; the carbonic anhydride (and also any sulphurous anhydride or halogens) is readily absorbed by a solution of an alkaline hydrate, so that pure nitrogen remains, and can be estimated by measurement. The single difficulty of this method is the complete removal from the apparatus of the indifferent gases of the air before the commencement of the combustion. This can be effected by complete exhaustion by the mercurial air pump, or more simply by a stream of carbonic anhydride. The procedure is as follows :—A combustion tube (fig. 8), about one metre long, has placed in it next to its closed ends about 30 grains of hydric sodic carbonate (*a b*), then a layer of cupric oxide (*b c*), then the mixture of the weighed substance and cupric oxide (*c d*), a layer of cupric oxide (*d e*) added, and the rest of the tube filled with copper turnings of clean metallic surface; a gas delivery tube is then attached by means of a perforated cork. The tube so filled (*a b*, fig. 9) is laid in the furnace, united to the bent delivery tube (*c f*), and the end of the latter dipped under mercury. One-half of the hydric sodic carbonate is then heated to brisk decomposition; the evolved gases, carbonic anhydride and water vapour, expel the air contained in the apparatus, which escapes in bubbles through the mercury. From time to time samples of the escaping gas are collected in a test tube completely filled with potash solution and mercury; when such a sample is absorbed by the potash without leaving any residue, it is certain that the air has been completely expelled. A measuring tube filled with mercury, first having about 50–60 cc. of concentrated potash solution run up into it, is placed over the end of the delivery tube and the combustion commenced. The cupric oxide at *d e* and *b c*, and the metallic copper at *e f* (fig. 8), are heated to bright redness, and the heating gradually carried to the mixture of cupric oxide and substance. As soon as the whole tube between *b* and *f* is red hot the evolution of gas ceases. All the organic substance is then burnt, and the greater part of the products of combustion collected in the measuring tube. The remaining portion of the hydric sodic carbonate is then heated, in order to displace any nitrogen remaining in the tube. After some time, when the complete absorption of the carbonic anhydride by the potash solution is quite certain, a small porcelain capsule is placed

FIG. 8.

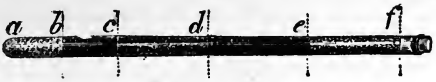
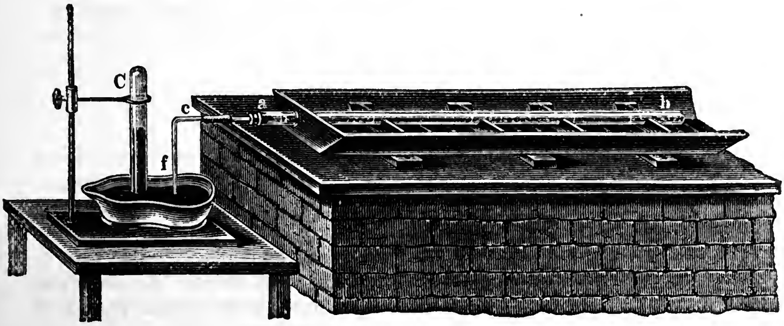


FIG. 9.

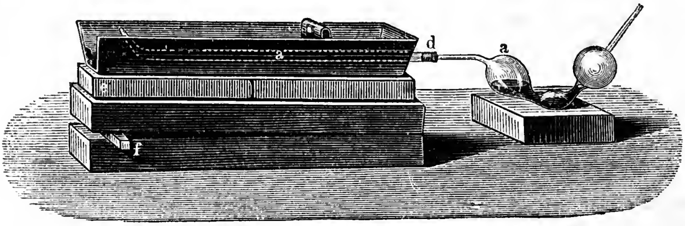


under the open end of the measuring tube, and the tube and contents removed to a deep cylinder filled with distilled water, the capsule being then removed. The mercury and potash sink out of the tube and are replaced by water. The measuring tube is now sunk so far into the cylinder that the surface of the water stands at the same level inside and outside the tube. It is then allowed to stand until both gas and water have acquired the temperature of the room; the volume of the gas in cubic centimetres (v) is then read off the tube, and at the same time the temperature (t C.) and the barometer (b in mm.) noted. The weight of nitrogen obtained is then, with correction for the tension of aqueous vapour (w in mm.)—

$$= \frac{v(b-w)}{760(1+0{\cdot}00367t)} \times 0{\cdot}0012562.$$

16. *Estimation of Nitrogen as Ammonia.*—As already explained, most organic bodies, when heated with alkaline hydrates, give off all their nitrogen as ammonia. The analysis is usually conducted as follows:—The substance to be analysed is mixed with five to six times its weight of soda lime in a warm porcelain mortar, and then transferred to a combustion tube which has already been drawn out to an oblique point and partly filled with soda lime; the mortar is then washed out with fresh soda lime and the tube nearly filled therewith, a plug of asbestos put lightly in, and a bulb apparatus containing hydrochloric acid fixed on by means of a well-fitting cork. The tube *a* (fig. 10) is then heated from the anterior backwards. Ammonia is evolved, which is absorbed by the acid, being converted into ammonic chloride. Free hydrogen and hydrocarbons are generally also evolved, the latter colouring the liquid in the bulb. At the close of the combustion, when the mass, which blackens at first, must have become quite white again, the point of the tube is broken off and air sucked through in order to bring all the ammonia into the bulb. This latter is then removed, the contents emptied into a porcelain basin, and the bulb rinsed repeatedly with pure water. The acid and wash waters are then mixed with excess of platinic chloride and the whole evaporated to dryness on the water bath. The residue consists of ammonic platinic chloride, $N_2H_8Cl_6Pt$, together with excess of platinic chloride. This latter is dissolved out by a mixture of alcohol and ether, and the insoluble ammonic platinic chloride collected on a dried and weighed filter, completely washed with ether alcohol, and dried at

FIG. 10.



100° until constant in weight. Every 100 parts of the double salt contain 6·28 parts of nitrogen. The double salt on ignition leaves a residue of platinum, which can be weighed; every atom of platinum found corresponds to two atoms of nitrogen, or 100 parts of platinum obtained corresponds to 14·172 parts of nitrogen.

Many organic substances, when heated with alkalies, give their nitrogen—at least in part—not as ammonia but in combination with carbon and hydrogen, in the form of organic bases, whose hydrochlorides give with platinic chloride compounds resembling the ammonic double salt, in which there is still one atom of platinum to two of nitrogen. It is, therefore, advisable always not only to weigh the double salt, but also the platinum left on ignition, the nitrogen being finally calculated from the latter.

16*b*. Instead of estimating by precipitating as above, the contents of the bulb may be evaporated to dryness and the chlorine in the residual ammonic chloride determined by addition of a standard solution of argentic nitrate; one atom of nitrogen must have been present for every atom of chlorine found.

Estimation of the Halogens.

17. In all cases where organic halogen compounds are not directly decomposed by water with complete conversion of the halogen into its hydro-acid (as happens with the chlorine, bromine, &c., compounds of the organic acid radicals), the halogens must be rendered capable of precipitation with argentic nitrate by the action of energetic reagents.

This can frequently be accomplished by the action of sodium amalgam upon an aqueous solution of the organic body, e.g. monochloracetic acid is decomposed according to the equation:

$$C_2H_3ClO_2 + Na_2 = C_2H_3NaO_2 + NaCl,$$

the chlorine being then readily precipitated from the sodic chloride by addition of silver salts.

In cases where this method is not available the decomposition can be effected by heating with pure lime in a combustion tube. The apparatus is quite similar to that used in estimating nitrogen as ammonia, only no absorption tube is required. The ignited residue is dissolved in nitric acid, precipitated with silver solution, the silver salt collected on a filter, washed, ignited, and weighed. As in this operation a large excess of lime must be employed a considerable volume of liquid is obtained, which makes the filtration a very wearisome operation.

Latterly this method has been nearly entirely superseded by another, which consists in the complete oxidation of the organic body by nitric acid at high temperatures. In many cases this reagent can be used dilute (1·2–1·3 sp. gr.), and acts completely even at 130°–150°; very few organic bodies can resist the action of fuming nitric acid at 180°–200°. The employment of temperatures so much above the boiling point of nitric acid necessitates the use of strong walled, sealed tubes, in order to resist the high pressures produced.

The substance for analysis is sealed up in thin glass bulbs, usually with bent, and therefore easily broken, capillary tubes. It is then enclosed, together with excess of argentic nitrate and of moderately concentrated, or if necessary of fuming, nitric acid, in a strong walled glass tube, care being taken that in sealing the drawn-out point is well thickened. Fig. 11 shows the whole apparatus. The glass bulb is now broken by vigorous shaking, the enclosed substance coming in contact with the nitric acid, and the tube is then heated for several hours in an air bath, heated to the necessary temperature. The air bath usually employed is shown in fig. 12; it contains several wrought-iron tubes closed at one end, and which are placed in an inclined position in the bath. If one of the glass tubes explodes, it cannot destroy the other tubes being heated in the bath at the same time, nor can it damage the operator.

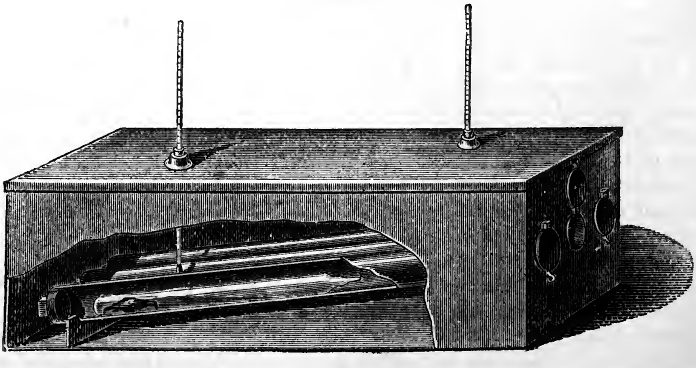
FIG. 11.

When the reaction is completed the apparatus is allowed to cool, the glass tube carefully removed, wrapped in a cloth, except the capillary tube, and the latter softened in a flame. The internal pressure blows the point out, and the strongly compressed gases (carbonic anhydride and reduction products of nitric acid) are evolved without danger. The glass tube is then cut open, the contents completely washed into a beaker, and after sufficient dilution of the nitric acid, the haloid silver salt, and the fragments of the glass bulb collected on a filter, washed, dried, ignited, and weighed. By subtraction of the weight of the filter, ash, and glass bulb the weight of the chloride, bromide, or iodide of silver is obtained, from which the weight of halogen can be calculated.

Estimation of Sulphur and Phosphorus.

18. Many sulphurised organic bodies can be completely oxidised by nitric acid, with conversion of their sulphur into sulphuric acid, the method above described being employed, the sulphuric acid being precipitated as baric sulphate from the largely diluted oxidation product. If halogens are estimated in the same operation the filtrate from the silver precipitate must be treated with hydrochloric acid, so as to remove all silver before precipitating the sulphuric acid.

FIG. 12.



If the substance oxidised by nitric acid contained phosphorus, arsenic, or metals, they will be converted respectively into phosphoric acid, arsenic acid, or metallic nitrates, and can be estimated according to the usual methods of quantitative analysis.

Frequently organic sulphur compounds resist the action of nitric acid, so that their decomposition can only be effected by fusion with nitre and an alkaline carbonate. The mixture must be made in such proportions that there shall be no explosion on heating. Volatile substances are generally partly oxidised in a sealed glass tube by nitric acid, whereby non-volatile bodies are formed; the acid liquid is then more than saturated with dry alkaline carbonate, and the whole evaporated to dryness and fused in a platinum dish. As soon as all carbon is burnt, and the mass has become completely white, it is allowed to cool, dissolved in water, and the sulphuric acid precipitated.

Estimation of Oxygen.

19. Oxygen is usually estimated indirectly; the sum of the percentages of the other elements present is deducted from one hundred, and the difference taken as oxygen. For instance, the combustion of 0·3 gram of cane sugar, which contains carbon, hydrogen, and oxygen only, gave 0·463 gram carbonic anhydride and 0·170 gram water. This, calculated into percentages, gives—

Carbon =	42·10
Hydrogen =	6·43
Sum	48·53
Oxygen (loss)	51·47
	100·00

DETERMINATION OF THE CHEMICAL FORMULÆ OF ORGANIC COMPOUNDS.

20. The results of the elementary analysis of an organic body are always expressed in percentages; from these empirical formulæ can be obtained by dividing the percentage number by the atomic weight of the element to which it refers, the quotients then expressing the proportions in which the atoms of carbon, hydrogen, oxygen, &c., are united to each other. These quotients, generally consisting of fractions, are reduced to the nearest round numbers, and then represent the empirical formulæ of the body.

In chemical analysis, as generally in any operation involving measuring or weighing, there are slight deviations from accuracy. A formula so obtained is still admissible, although the percentage numbers calculated from it do not quite agree with those found in the investigation, provided that the deviation does not exceed a certain limit. This limit of error is found to be about 0·3 per cent. for carbon and 0·2 per cent. for hydrogen; for instance, in the combustion of pure glacial acetic acid the following numbers were obtained:—

Carbon	39·82
Hydrogen	6·75
Oxygen	53·43
	100·00

These being divided by the respective atomic weights, the quotients will express the ratio of the elementary atoms in the compound.

$$\text{For carbon } \frac{39{\cdot}82}{12} = 3{\cdot}318$$

$$\text{For hydrogen } \frac{6{\cdot}75}{1} = 6{\cdot}75$$

$$\text{For oxygen } \frac{53{\cdot}43}{16} = 3{\cdot}339$$

If these are now reckoned to 1 atom of carbon they give—

$$\text{To 1 atom carbon } \quad C_1$$

$$\text{Hydrogen } \frac{6{\cdot}75}{3{\cdot}318} = H_{2{\cdot}034}$$

$$\text{Oxygen } \frac{3{\cdot}339}{3{\cdot}318} = O_{1{\cdot}006}$$

or as nearly as can be expected with unavoidable errors, to the empirical formula CH_2O, from which the following percentage composition is calculated :—

$$\begin{aligned} C &= 40{\cdot}00 \\ H &= 6{\cdot}67 \\ O &= \underline{53{\cdot}33} \\ & 100{\cdot}00 \end{aligned}$$

Determination of the Molecular Formula.

21. The chemical formula of a body must be something more than the mere expression of its percentage composition; it should in addition express the atomic composition of the smallest, relatively, existing quantity of the body, its molecule. It is evident that the latter can be any whole multiple of the empirical formula; the acetic acid molecule may probably be $C_2H_4O_2$, $C_3H_6O_3$, &c.

In order, therefore, to find the true chemical formula of a body, in addition to the percentage composition there must also be determined the relative weight of its molecule, either from certain physical qualities, especially the vapour density (see further on), or from the products derived from it by chemical changes.

Of these latter 'derivatives' the most important for acids and bases are their salts; for indifferent bodies, especially those that contain only carbon and hydrogen, their haloid substitution products, i.e. derivatives in which the hydrogen is replaced by a halogen.

22. When acetic acid, for instance, is converted into its silver salt by boiling with argentic oxide, and the salt then submitted to analysis, it gives the following percentage composition :—

C	14·28
H	1·85
Ag	64·82
O	19·05

and calculating from these the atomic proportions—

$$C = \frac{14{\cdot}28}{12} = 1{\cdot}19 \quad \frac{1{\cdot}19}{{\cdot}6} = 1{\cdot}98 = 2$$

$$H = \frac{1{\cdot}85}{1} = 1{\cdot}85 \quad \frac{1{\cdot}85}{{\cdot}6} = 3{\cdot}08 = 3$$

$$Ag = \frac{64{\cdot}82}{108} = 0{\cdot}60 \quad \frac{{\cdot}6}{{\cdot}6} = 1{\cdot}00 = 1$$

$$O = \frac{19{\cdot}05}{16} = 1{\cdot}19 \quad \frac{1{\cdot}19}{{\cdot}6} = 1{\cdot}98 = 2$$

The simplest formula for argentic acetate is

$$C_2H_3AgO_2$$

and requires for acetic acid a molecular formula at least as large as $C_2H_4O_2$, i.e. double the empirical formula previously determined.

Several other substances have the same percentage composition as acetic acid, although with dissimilar properties ; such are dried grape sugar, lactic acid, &c. The analysis of derivatives of these bodies, however, leads to completely different molecular formula.

The silver salt of lactic acid, e.g., gives this latter the formula $C_3H_6O_3$, as it contains three atoms each of carbon and oxygen and five atoms of hydrogen to one atom of silver.

	Found per Cent.	Atomic Quotient	To 1 atom Ag	
			Found	Calculated.
C	18·36	1·530	3·02	3
H	2·50	2·500	4·94	5
Ag	54·65	0·506	1·00	1
O	24·49	1·531	3·03	3

23. In order to determine the molecular formula of an organic base it is analysed both in the free state and in form of the salts which it yields with acids—most simply with hydrochloric acid. Bearing in mind that organic bases, or alkaloids, resemble ammonia in their chemical behaviour, i.e. unite with acids without separation of water, it is easy from the composition of the salt to deduce that of the base.

As an example the formula of the hydrochloride compound of creatinine may be calculated. On elementary analysis it gave in per cents.—

Carbon	32·48
Hydrogen	5·30
Nitrogen	28·27
Chlorine	23·41
Oxygen	10·54

On calculating this to 35·5 parts, or one atom, of chlorine there was found—

Carbon 48 = 4 × 12 = 4C
Hydrogen 8 = 8 × 1 = 8H
Nitrogen 42 = 3 × 14 = 3N
Chlorine 35·5 = 1 × 35·5 = 1Cl
Oxygen 16 = 1 × 16 = 1O

The formula of creatinine hydrochloride is therefore $C_4H_8N_3OCl$. On subtracting HCl from this we get for creatinine itself $C_4H_7N_3O$, with which formula the results of the analysis of free creatinine are in agreement.

		Calculated.	Found.
C_4	48	42·48	42·54
H_7	7	6·19	6·38
N_3	42	37·17	37·20
O	16	14·16	13·88
1 molecule creatinine	113	100·00	100·00

24. As the so-called indifferent bodies—i.e. such as are neither of acid nor basic nature—do not enter into combination, it is necessary, in determining their molecular weight, to have recourse either to splitting up—i.e. decomposition into several other compounds of known molecular formulæ, whose relative quantities are then determined—or to substitution.

The analysis of acetic ether, e.g., gives as its empirical formula C_2H_4O; by treatment with potash solution, however, it splits up into equal molecules of ethyl alcohol, C_2H_6O, and potassic acetate, $C_2H_3KO_2$. It is therefore seen that the above expression must be doubled in order to get four carbon atoms. The decomposition is then represented by the equation:

$$C_4H_8O_2 + KOH = C_2H_6O + C_2H_3KO_2.$$

25. The simplest formula derivable from the analysis of benzene is CH. A crystalline compound of benzene and chlorine appears to confirm this, as its investigation leads to the formula CHCl. When heated with alcoholic potash, however, it is converted into an oil, which to one chlorine atom contains two carbon and one hydrogen atoms.

From this the benzene formula would be C_2H_2, the chlorine compound $C_2H_2Cl_2$, the decomposition product C_2HCl. By the investigation of other products of the action of chlorine upon benzene, C_2H_2 proves not to be its formula. One of these bodies contains three carbon atoms to one chlorine atom $= C_3H_2Cl$. The composition of another corresponds to C_3HCl_2. Already these derivatives with both two and three carbon atoms require the presence of C_6 in the molecule, and apart from that other substitution products exist that cannot be otherwise formulated.

From the empirical formula of the chlorine derivatives the following series of molecular formulæ of benzene derivatives is obtained:—

	Empirical Formula.	Molecular Formula.
Benzene	CH	C_6H_6
Chlorine compound	CHCl	$C_6H_6Cl_6$
First chlor substitution product	C_6H_5Cl	C_6H_5Cl
Second " " "	C_3H_2Cl	$C_6H_4Cl_2$
Third " " "	C_2HCl	$C_6H_3Cl_3$
Fourth " " "	C_3HCl_2	$C_6H_2Cl_4$
Fifth " " "	C_6HCl_5	C_6HCl_5
Sixth " " "	CCl	C_6Cl_6

Derivation of the Molecular Weight from the Vapour Density.

26. The fact that in the union of gases the volumes stand in very simple relation to each other and to the volume of their gaseous compound, led at the beginning of this century to the view that equal volumes of different gases and vapours contain, under like conditions of temperature and pressure, an equal number of molecules. This has since been amply confirmed, and now forms one of the most important fundamental laws of physical chemistry.

The weights of equal volumes of different gases, under like temperature and pressure (the gas and vapour densities), express directly the relative weights of the molecules. The molecular weight of any gaseous or volatile (without decomposition) body is found by multiplying the experimentally determined density on the air scale (i.e. air = 1) by 28·92—i.e. the molecular weight is 28·92 times as great as the density of the gas or vapour on the air scale.

	Density Found.	Density × 28·92.	Molecular Weights.
Hydrogen	·0692	2·00	2·0
Hydrochloric acid	1·274	36·84	36·5
Ammonia	·589	17·03	17·0
Water	·622	17·99	18·0
Benzene	2·675	77·36	78·0

Relatively small errors in the determination of the vapour density would lead to not inconsiderable deviations in the molecular weight obtained by this method; but as the molecular weight must be a whole multiple of the empirical formula, the results are quite sufficiently near to leave no doubt as to which multiple is the correct one.

Determination of Vapour Density.

27. The density of a gas or vapour is the quotient of a given volume thereof divided by the weight of an equal volume of atmospheric air at the same temperature and pressure. As a cubic centimetre of atmospheric air weighs ·0012932 grm. at 0° and 760 mm. pressure, according to the laws of Marriotte and Gay-Lussac, the weight (in grammes) P of any given volume V (in cc.) at any given temperature t and pressure b can be calculated by the formula

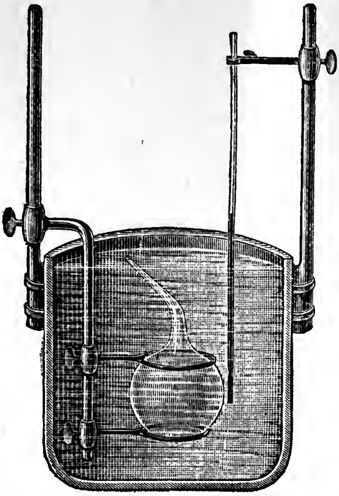
$$\text{P} = {\cdot}0012932 \cdot \frac{1}{1 + {\cdot}00367t} \cdot \frac{b}{760}\ \text{V}.$$

There is only required, therefore, in the estimation of a vapour density, the weight P′ and the corresponding volume V′ at the temperature t and pressure b of the gaseous or vapourisable body. There are two different methods employed for this purpose: either the amount required to fill a flask of known capacity at a known temperature and pressure is *weighed*, or the volume occupied by a known weight of the vapour is *measured*.

28. In order to estimate the density according to the first principle, a glass balloon of about 300–500 cc. capacity is employed; the neck is drawn out to a long capillary tube, and bent at an obtuse angle.

The flask is dried by repeated exhaustion and admission of dried air, and then weighed full of dry air, the temperature *t* and pressure *b* being noted. About 5–10 grm. of the liquid under examination is introduced into the slightly warmed balloon, which is then placed in an oil bath, heated to a few degrees above the boiling point of the substance, as shown in fig. 13. The thermometer must be so placed in the oil that its bulb is as high as the middle of the balloon and as near as possible to it. The air is expelled by the vapour formed, the excess of the latter also escaping. When this ceases the temperature is raised about 20°–30°; the portion of the capillary tube projecting above the oil being also heated, to volatilise any liquid condensed there; the point fused in the blowpipe flame, the temperature *t*, and the pressure *b* being noted at the same time. The balloon is now removed from the oil bath, carefully cleaned, and when cold weighed. The next point is to ascertain the capacity of the balloon and the volume of any air left in it. The point is, therefore, broken off under mercury, whereupon the balloon fills with the metal. If a gas bubble of sufficient size to affect the result is visible, it is transferred to a graduated tube placed over mercury, and its volume and weight determined, calculated also to the temperature of the bath and pressure at the time of fusing, and both numbers used for the correction of the weight and volume of the vapour.

Fig. 13.



The balloon, after completely filling with mercury, is then emptied into a graduated vessel, in order to determine its capacity at the ordinary temperature. The following data for the calculation of the vapour density are now obtained :—

P weight in grammes of the balloon filled with air at the temperature *t* and the pressure *b*.

P′ weight in grammes of the balloon filled with vapour at the temperature *t*′ and the pressure *b*′.

V capacity of the balloon at the temperature *t*.

From these the weight *p* of the atmospheric air in the balloon at $t°$ and *b* mm. pressure is thus calculated.

$$p = \cdot 0012932\,\text{V} \,.\, \frac{1}{1 + \cdot 00367t} \cdot \frac{b}{760}$$

The weight of the glass of the balloon is $\text{P} - p$, that of the vapour therefore $\text{P}' - (\text{P} - p)$.

The glass expands on heating; therefore the capacity V′ of the balloon at the temperature t' is, if k be the coefficient of cubic expansion of the glass (free from lead = ·00255)—

$$\mathrm{V}' = \mathrm{V}\,(1 + k\,t').$$

Therefore the weight of an equal volume of air under like circumstances

$$= \cdot 0012932 \,.\, \mathrm{V}\ [1 + k\,t'] \,.\, \frac{1}{1 + \cdot 00367t'} \,.\, \frac{b'}{760}$$

the vapour density D of the body being (without correction for any residual air in the balloon)

$$\mathrm{D} = \frac{\mathrm{P}' - (\mathrm{P} - p)}{\cdot 0012932 \,.\, \mathrm{V} \,.\, (1 + k\,t') \,.\, \dfrac{1}{1 + \cdot 00367t'} \,.\, \dfrac{b'}{760}}$$

29. Two important methods based upon the second principle are now in use—viz. the methods of Hoffmann and Victor Meyer, which are based upon the method of Gay-Lussac, now seldom used.

Hoffmann's method is applicable to bodies whose boiling point is considerably below 100° C., and whose vapours already follow the laws of Marriotte and Gay-Lussac at the boiling point of water. This excellent method may also be used for the vapour density determination of less volatile bodies, as by the employment of a torricellian vacuum accurate measurements of the volumes may be made at a much lower temperature than the body's actual boiling point under atmospheric pressure.

A graduated barometer tube about 1 metre long *a* (fig. 14) is completely filled with dry mercury and inverted in a vessel full of mercury. The tube is then surrounded by a wider tube *b*, fitted tightly to it by the cork *c*. At the upper end of this surrounding tube a tube *d* is fitted for the entrance of vapour, whilst an exit tube, united to a condenser, is attached to its lower end.

A small bottle of 1 cc., or less, content, provided with a glass stopper, is completely filled with the substance under investigation, and the weight P of the contents determined by weighing. The bottle is then sent up the barometer tube, when the stopper is generally expelled by the excess of interior pressure. A good stream of the vapour of some substance of known boiling point is then passed through the annular space between the cylinder and measuring tube, by which the latter and its contents are soon raised to a like temperature.

The substances generally used in the vapour bath are water for the more volatile and aniline for the less volatile bodies.

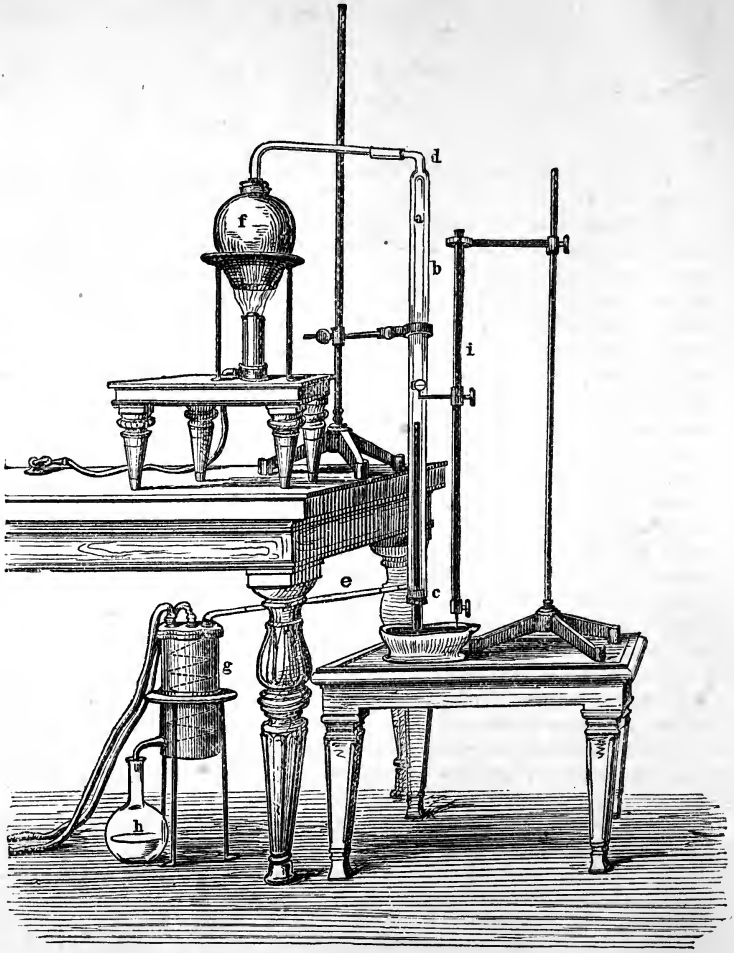
The liquid contained in the bottle is converted into vapour, depressing the mercurial column. As soon as this has reached a constant position in the measuring tube the volume of vapour V is read off, together with the atmospheric barometric pressure B, the height H of the mercurial column inside the measuring tube and the boiling point of the liquid used for the vapour bath being also noted. When aniline or other high-boiling liquids have been employed, the pressure on the vapour at the temperature t is not simply = B − H, the interior mercurial column being considerably heated and its sp. gr.

thereby diminished. The height must therefore be calculated to the temperature t' of the exterior air; this may be accomplished approximately by the formula

$$\text{H}' = \text{H}\,[1 - \cdot 00018\,(t - t')]$$

A correction must also be made for the tension of the mercurial

Fig. 14.



vapour T. This has been determined by Regnault, and can be read off directly from his tables.

The pressure which the vapour exerts is therefore

$$\text{B} - \text{H}' - \text{T}.$$

The weight of an equal volume of air under the same condition is

$$= \cdot 0012932 \cdot \text{V} \cdot \frac{\text{B} - \text{H}' - \text{T}}{(1 + \cdot 00367t)\ 760}$$

and the vapour density

$$\text{D} = \frac{\text{P}\ (1 + \cdot 00367t)\ .\ 760}{\cdot 0012932\ .\ \text{V}\ (\text{B} - \text{H}' - \text{T})}$$

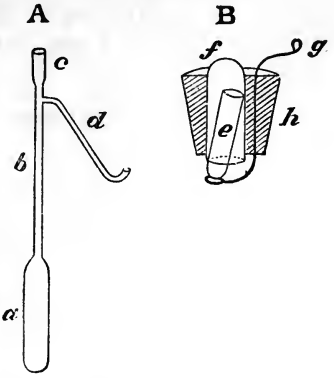
30. A more recent method, that of Victor Meyer, allows of the density of bodies being very accurately determined within very wide ranges of temperature.

The principle of the process is similar to that of Hoffmann's, and consists in comparing the weight of an equal volume of air with that of the substance in the gaseous state.

The apparatus employed is shown in fig. 15.

The bulb *a* of the vapourisation tube A is immersed in a cylindrical vessel containing a liquid to serve as bath; this latter is heated until a constant temperature is attained, when the substance—about ·1 grm.—previously weighed in the small tube *e*, 10 to 20 mm. long and 2 to 4 wide, and lightly held on the bent wire *g* passing through the cork of the vapourisation tube (shown on an enlarged scale at B, fig. 15), is allowed to fall to the bottom of the wide portion by slightly rotating the wire. As soon as the substance arrives at the heated portion of the tube, it passes into the vaporous state, and expels an equal volume of air by the side tube *d*, which is received in a measuring tube over water, and its amount read off, temperature and pressure being noted.

Fig. 15.



The temperature in the vapourisation tube need not be accurately known, only that it be sufficiently high for the whole of the substance to be in a gaseous state.

For very high temperatures the wide portion of the vapourisation tube must be of platinum or porcelain, and the bath, instead of water, aniline, &c., may be melted lead, or for the highest temperatures a small reverberatory gas furnace.

The abbreviated formulæ

$$\text{D} = \frac{\text{S}\ .\ 760\ (1 + \cdot 003665t^\circ)}{(\text{B} - w)\ \text{V}\ .\ \cdot 0012932}$$

where D = density sought,
S = weight of substance used,
(B − *w*) = barometer minus tension of water vapour at *t*°, the temperature of observation reduced to 0° C.,
V = volume air in c. centim.,

·0012932 = weight of 1 cc. air at 760 mm. B and 0° C.,
$t°$ = temperature of room or air in measuring tube,

will give the required density with sufficient accuracy.

RATIONAL FORMULÆ AND ORGANIC RADICALS.

31. The molecular formula of an organic compound shows which elements and what number of atoms of each are contained in the molecule, without expressing the order and method of their union.

The study of chemical changes shows that in the greater number of organic molecules, atoms of any ingredient elements can be replaced—singly or in groups—with differing ease, by other elementary atoms, or eliminated without replacement, and that they must be united with varying degrees of firmness. In order to express this fact in the formula, the symbols of the respective elements are not written once only, but repeated as frequently as may be required to indicate the varying degrees of firmness of union. The number of atoms in each particular form of union are expressed in the usual manner. Formulæ modified in this way are termed *rational formulæ.*

In such rational formulæ there must evidently exist some groups of atoms which suffer no change during a given reaction; such an unattacked residue or constituent common to both the original and derived body is termed a radical, and when it contains carbon it is termed an organic radical or residue.

An example will easily demonstrate these statements. Ordinary (ethylic) alcohol whose formula is

$$C_2H_6O$$

gives up one of its six hydrogen atoms when treated with sodium, being thereby converted into the body C_2H_5NaO. In this reaction the group C_2H_5O remains unchanged, and is therefore the radical of ethylic alcohol, and the rational formula would be

$$C_2H_5O.H.$$

This body is, however, capable of further changes; by treatment with ozone or with easily reducible bodies, it loses two hydrogen atoms, without replacement, being converted into aldehyde, C_2H_4O, which can further take up an additional atom of oxygen, yielding acetic acid. From this the rational formula of alcohol is

$$C_2H_4O.H_2,$$

in which the group C_2H_4O appears as the radical.

By numerous decompositions groups of different elementary atoms are simultaneously removed from the original compound. By the action of hydrochloric acid, alcohol is changed into the body C_2H_5Cl and water, having its oxygen atom, together with one of the hydrogen atoms, removed, and only a single chlorine atom entering in their place. This reaction leads to the formula

$$C_2H_5.OH,$$

in which the organic radical C_2H_5 (ethyl) is united to the inorganic radical OH (hydroxyl).

An organic compound can have in this way *different rational formulæ*, corresponding to the different methods in which it suffers decomposition. Rational formulæ of such a kind are only reaction or *decomposition formulæ.*

Both the reaction formulæ for ethylic alcohol, $C_2H_5.OH$ and $C_2H_5O.H$, can be united into the single formula

$$C_2H_5.O.H,$$

from the fact that the atom of hydrogen replaced by sodium, is no other than the one which is expelled simultaneously with oxygen by action of hydrochloric acid.

$$C_2H_5.O.H + Na = C_2H_5.O.Na + H$$
$$C_2H_5.O.H + HCl = C_2H_5.Cl + HOH.$$

By this the united rational reaction-formulæ obtain a further significance. The actual connection of this hydrogen atom to the oxygen atom can only be that both are united together, that the monad H is united to the organic residue C_2H_5 by means of the dyad O. The rational formula $C_2H_5.O.H$ expresses the order of combination of at least two atoms in the alcohol molecule, as well as certain decomposition possibilities, and becomes therefore a *constitutional formula.*

Similarly to the oxygen and one hydrogen atom of the ethylic alcohol, the method of union of the elements composing the radical C_2H_5 may be settled by the study of reactions of greater extent, not alone by decomposition processes, but also by the reverse—*synthesis,* the building up of the organic compound from simpler bodies, or even from its constituent elements.

Alcohol, as already mentioned, is converted by oxidation into acetic acid, $C_2H_4O_2$. In this, by treatment with phosphoric chloride, one hydrogen and one oxygen atom are replaced by one chlorine atom, the body C_2H_3OCl being formed. Acetic acid has, therefore, the hydrate formula $C_2H_3O.OH$. If its sodic salt $C_2H_3O.ONa$ be submitted to dry distillation with sodic hydrate, NaOH, a residue of sodic carbonate, is left, and marsh gas, CH_4, is evolved. According to the equation:

$$C_2H_3O.ONa + NaOH = CO_3Na_2 + CH_4$$

the sodic carbonate obtaining CO_2Na, the marsh gas CH_3, from the sodic acetate. The reaction is expressed completely in accordance with the facts by the rational formulæ:

$$CH_3-CO.ONa + HONa = CH_3H + CO.ONa.ONa.$$

From this it is highly probable that in acetic acid three hydrogen atoms are united to one carbon atom, the two oxygen atoms, and by means of one of them the fourth hydrogen atom, to the other carbon atom. Numerous other reactions lead to the same conclusion.

The detailed constitutional formula obtained for acetic acid in this way, leads to the further conclusion that in ethyl alcohol also the same group, CH_3, must occur, and makes it probable that the constitutional formula is $CH_3.CH_2.OH$. Complete confirmation of this view is obtained in the synthesis of ethyl alcohol from marsh gas. On exposing a mixture of this gas and chlorine to diffused daylight, there results, with elimination of one of the four hydrogen atoms, the the body CH_3Cl, methylic chloride:

$$CH_4 + Cl_2 = CH_3Cl + HCl,$$

which by heating with potassic cyanide yields potassic chloride and methylic cyanide:

$$CH_3Cl + KCN = KCl + CH_3.CN.$$

Nascent hydrogen converts the latter into ethylamine:

$$CH_3.CN + 4H = CH_3.CH_2.NH_2,$$

in which, by action of nitrous acid, the amide group NH_2 may be replaced by hydroxyl, OH:

$$CH_3.CH_2.NH_2 + NO.OH = H_2O + N_2 + CH_3.CH_2.OH,$$

the product obtained being ethylic alcohol.

The constitutional formula obtained in this way not only makes clear all the known reactions of alcohol, but shows at the same time in what order the component atoms must be united amongst themselves, or, in other words, it expresses the constitution of the compound radicals of the less detailed rational formula. Therewith it helps to a large extent to the solution of one of the most important questions of chemical knowledge—*from the nature and position of the component elementary atoms to determine the properties of a compound.*

Constitutional formulæ which show in this way the relative positions of all the atoms in the molecule of a compound are termed *structural formulæ.* They are based upon the intrinsic presupposition of the valency of the chemical elements.

OUTLINES OF THE CHEMICAL STRUCTURE OF ORGANIC BODIES.

32. The groundwork of every organic molecule is the tetrad carbon atom.

By the saturation alone of the four bonds of a single carbon atom by all possible other mono- or polyvalent elementary atoms, a very large number of organic compounds will result, which are known as the mono-carbonides. We know that nearly all elementary atoms are able to combine not only with those of other elements, but also to unite amongst themselves. Monad elements form their free molecules in this way, which in the undecomposed state are incapable of further direct combination: e.g. H—H hydrogen gas, Cl—Cl chlorine gas.

On the other hand, when two atoms of a polyvalent element unite with each other, it may be by employment of their total attraction possibilities, e.g.

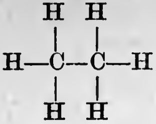
$$O=O \text{ oxygen gas,}$$

or only a part of it is employed for this purpose, whilst the other parts are available for union with other elements, e.g.

$$H—O—O—H \text{ hydric peroxide.}$$

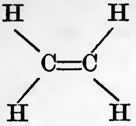
The higher the valency of an elementary atom, the more complicated and various will be its capability of uniting with other atoms of the same or other elements.

If two carbon atoms (in the dicarbonides) coalesce with employment of only one bond each, there remains to each atom three—together six—bonds disposable for union with other atoms, e.g.



$$\mathrm{H_3C{-}CH_3}$$

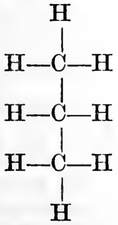
By union by means of two bonds, each has but two bonds left—



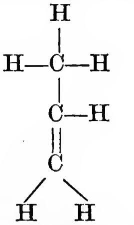
by trivalent union, each only one—

$$\mathrm{H{-}C{\equiv}C{-}H}$$

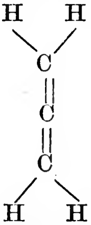
33. The number of carbon atoms directly united to one molecule can proceed far beyond two. There are carbon groups or 'carbon nuclei' which contain three (tricarbonides), four (tetracarbonides), five (pentacarbonides), and so on up to thirty or more carbon atoms, combined together. This, therefore, comes to the fact that a carbon atom may be united to several others with only partial saturation of their bonds. In this relation the union of a carbon atom with only one other is distinguished as union of the first order, or primary union, which may be mono-, di-, or trivalent. The combination of an atom with two others forms a union of the second order, or secondary union—



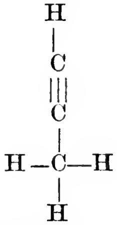
Secondary monovalent union.



Secondary mono- and divalent union.

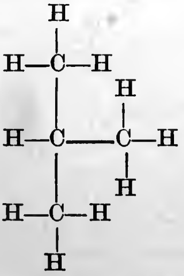


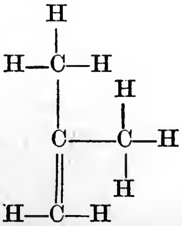
Secondary di- and divalent union.



Secondary tri- and monovalent union.

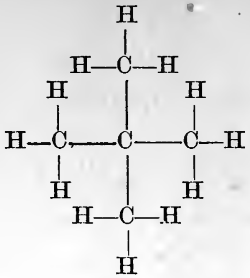
In the combinations of the third order, or tertiary unions, one carbon atom is in combination with three others—





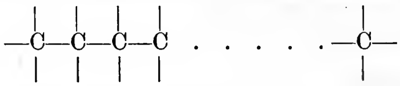
whereby the nucleus must contain at least four carbon atoms.

Finally, a carbon atom can be in combination with four others, forming a combination of the fourth order, or quaternary union—

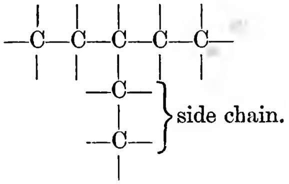


This requires a nucleus of at least five carbon atoms.

34. When a nucleus contains primarily and secondarily combined carbon atoms only, it forms a simple open, so-called normal chain—

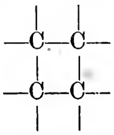


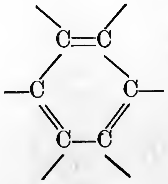
Side or secondary chains result when to one of the carbon atoms placed in the secondary position in a simple chain a third or fourth is united—



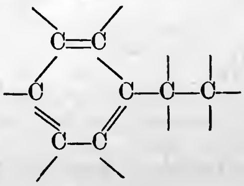
Primarily united carbon atoms can only occur at the end of chains; they are '*terminal*,' all others being '*intermediate*.'

If the terminal carbon atoms of a simple open chain also unite with one another so that the primary combination is completely lost, there results *closed chains* or *carbon rings*, e.g.





to which further side chains may be attached—

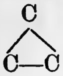


35. The greater the number of carbon atoms united to a nucleus in a molecule, the greater the number of carbon chains become. Whilst by only monovalvent combination two carbon atoms can form only one nucleus—

C—C

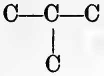
with three atoms there are two such possibilities—

C—C—C and

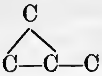


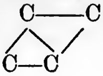
Four carbon atoms could form five nuclei—namely, two with open and three with closed chains—

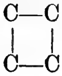
C—C—C—C



$\mathrm{C{-}\underset{\substack{|\\ C}}{C}{-}C}$

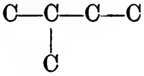




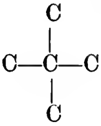


With five carbon atoms there are three possibilities with open chains—

C—C—C—C—C

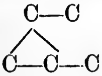


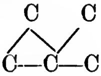
$\mathrm{C{-}\underset{\substack{|\\ C}}{C}{-}C{-}C}$

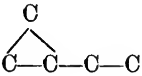


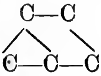
$\mathrm{C{-}\overset{\substack{C\\ |}}{\underset{\substack{|\\ C}}{C}}{-}C}$

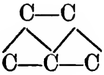
and seven with closed chains—

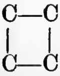


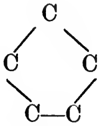










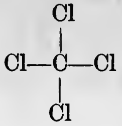


a total of ten, and so on in rapidly increasing progression.

The number of possible modifications of nuclei grows also considerably by the introduction of di- or trivalent union of the carbon atoms. In cases, therefore, where all the bonds not employed in nucleus-building are saturated by atoms of one and the same element, e.g. hydrogen, a very considerable number of organic bodies may exist having the same content of hydrogen and carbon atoms, but entirely differing properties, owing to the difference of their nuclei (isomeric compounds; see § 46).

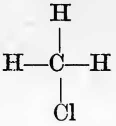
36. To a polyvalent nucleus (as to a polyvalent element) atoms of several different elements can be attached; the number of possible organic compounds is therefore enormous.

In hydrogen and carbon compounds the hydrogen atoms may be totally or partially replaced by those of another monad element. If chlorine is the replacing element we have, in addition to the body—

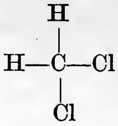


$$\mathrm{Cl{-}\overset{Cl}{\underset{Cl}{C}}{-}Cl}$$

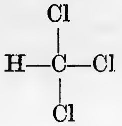
still three other monocarbonides containing hydrogen and chlorine—



$$\mathrm{H{-}\overset{H}{\underset{Cl}{C}}{-}H}$$



$$\mathrm{H{-}\overset{H}{\underset{Cl}{C}}{-}Cl}$$



$$\mathrm{H{-}\overset{Cl}{\underset{Cl}{C}}{-}Cl}$$

or CH_3Cl CH_2Cl_2 $CHCl_3$

and similarly also with bromine, iodine, &c., compounds.

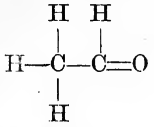
By attachment of three different monad elements such compounds are formed as

CH_2ClBr $CHBr_2I$

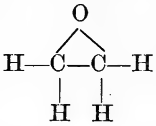
Possibly also a body may be formed—

$CHClBrI$.

37. When polyvalent elements unite with a carbon nucleus it may be either with their whole valency, e.g.

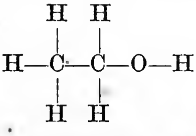


$$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{C}{=}O}$$

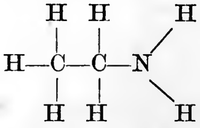


$$\mathrm{\overset{H}{C}{\equiv}N}$$

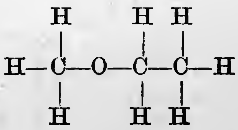
or with only a part. In this case the polyvalent elementary atom brings other elements into the compound with it—



$$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}O{-}H}$$

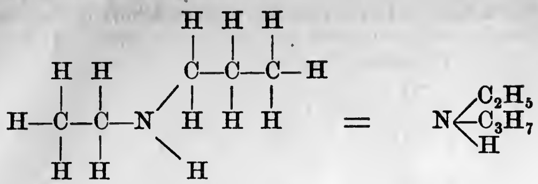


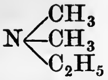
If the latter be not carbon, compounds of carbon nuclei with inorganic radicals will result (such as above with hydroxyl, HO—, amidogen, H_2N—). A polyvalent element can unite quite as well with one part of its valency to one carbon nucleus, and with the remainder to other carbon nuclei. Dyad elements can unite in this way with two carbon nuclei, e.g.



$$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}O{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}H}$$

Triads with two or three nuclei—

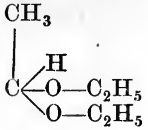




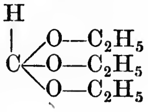
&c.

Organic bodies result in this way with more than one carbon nucleus.

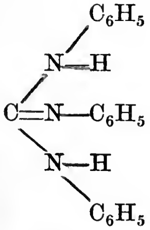
38. The number of nuclei held together in a molecule by a polyvalent element can, of course, exceed the valency of the respective elements, if there be several atoms of the same element attached to a single carbon nucleus by a part of their bonds, e.g.



oxide with three nuclei.



oxide with four nuclei.

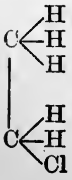


nitrogen compound with four nuclei.

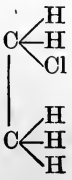
&c.

39. *Chemical Position.*—The nature of the compound of one and the same carbon nucleus with several other elements at the same time, depends not only on the relative number, but in many cases on their position relatively to the individual carbon atoms of the nucleus.

If a dicarbonide nucleus is united to only a single other elementary atom besides hydrogen atoms, it is quite indifferent to which of the two carbon atoms it is attached.

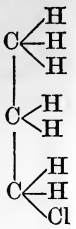


and

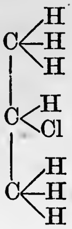


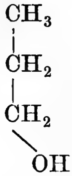
are identical.

So soon, however, as, by increase in the number of carbon atoms, the method of union of the individual carbon atoms differ, the order of partition is no longer without influence upon the character of the organic molcule. The molecules

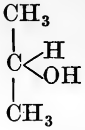


and



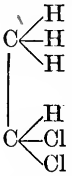


and

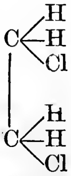


though consisting of like numbers of atoms of the same elements, are yet completely different bodies, as the chemical position of the chlorine atom or hydroxyl group is not of the same value in the first as in the second case.

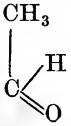
If a dicarbonide group has attached to it, besides hydrogen atoms, at least two other elementary atoms, or radicals, the order of distribution or chemical position of these will have influence. The structural formulæ



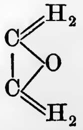
and



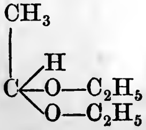
e.g., belong to two entirely different bodies of the general molecular formula $C_2H_4Cl_2$; similarly there exist the bodies of similar molecular composition but completely different properties—



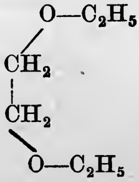
and



and again



and



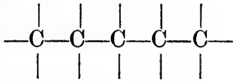
40. *Valency of the Carbon Nucleus.*—The valency or saturation capability of a carbon nucleus with which it unites to other elements, is expressed by the difference between the sum of the valency of the carbon atoms composing it, and the valency employed in their mutual union.

If the union is in the simplest way—i.e. if n carbon atoms with a total of $4.n$ bonds combine to an open chain, with mutual monovalent union only—there are then $n - 1$ bonds left, of which each corresponds to two attraction units. The valency of the nucleus is therefore

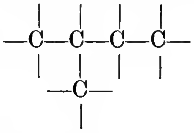
$$4n - 2(n - 1) = 2n + 2,$$

whether the chain is single or has side chains.

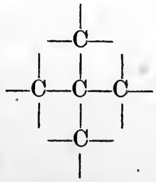
Another kind of consideration leads to the same result. In the simple open chain of n C there are two terminal carbon atoms, each with three, $n - 2$, intermediate atoms with two each, in sum a valency of $2 . 3 + 2(n - 2) = 6 + 2n - 4 = 2n + 2$ for attachment to other elements. The entry of side chains does not affect the result, because, though satisfying one valency of an intermediate carbon atom, its own terminal carbon atom, having a valency of three, makes the total additional valency $2n'$; e.g. for the different pentacarbonide nuclei with only monovalent union—

1. Nucleus 

Two terminal	C atoms with	$2 . 2 + 2$	available bonds
Three intermediate	,, ,, ,,	$3 . 2$	,, ,,
Total		$5 . 2 + 2 = 12$	,, ,,

2. Nucleus 

Three terminal	C atoms with	$3 . 2 + 3$	available bonds
One intermediate	,, atom ,,	$1 . 2$	,, ,,
,, ,,	,, ,, ,,	1	,, bond
Total five	,, atoms ,,	$4 . 2 + 4$ or $5 . 2 + 2$	bonds

3. Nucleus 

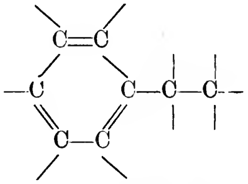
Four terminal	C atoms with	$4 . 2 + 4$	available bonds
One intermediate	,, atom ,,	0	,, bond
Total five	,, atoms ,,	$4 . 2 + 4 = 5 . 2 + 2$	bonds

For every divalent union of neighbouring carbon atoms the number of bonds used in the nucleus increases by two, the number of available bonds decreasing by two. In open chains, and where the divalent union occurs but once, the valency of the nucleus is $2n + 2 - 2 = 2n$, when the divalent union occurs twice, $2n + 2 - 2 \cdot 2 = 2n - 2$, &c.

From the same grounds, with bivalent union of neighbouring carbon atoms of the $2n + 2$ bonds originally available, four are used up, making the valency of the nucleus $2n - 2$.

Where by the union of two terminal carbon atoms a closed chain is formed, and the union is monovalent, two bonds are employed. If there results a single ring without side chains, and in which the union between the carbon atoms is monovalent only, the valency of the nucleus will be $2n$.

According to these principles the valency of every nucleus of known structure is easily determined, even though it contains many varieties of combination; e.g. for the nucleus containing eight carbon atoms



The valency can be easily calculated as follows:—

Possible maximum valency of a nucleus of 8 C .	$2 \cdot 8+2$
The closing of the ring diminishes it by . .	2
Three divalent unions „ „ . .	6
Total loss of available bonds . . .	8

There remains

$$2 \cdot 8+2-8=2 \cdot 8-6=10;$$

or for all nuclei of similar structure and n carbon atoms $2n-6$ as the valency.

41. *Valency of Compound Organic Radicals.*—The valency of an organic radical (the constituent common to both original substance and final product of a reaction) depends on the valency of the carbon nucleus and on the number of atoms attached thereto, and equals the difference between these two. If, for example, an open chain of monovalent union, and whose valency therefore is $2n + 2$, has united to it $2n + 1$ hydrogen atoms, there remains a single carbon bond to unite with other elements.

$$2n+2-(2n+1)=1.$$

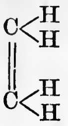
Radicals of the general formula C_nH_{2n+1} are therefore monovalent, those of the composition C_nH_{2n} divalent, &c.

If a compound radical contains united to its carbon nucleus not only monad elements, but also polyad elements, the method of union of the latter can often be settled by the empirically ascertained valency of the radical.

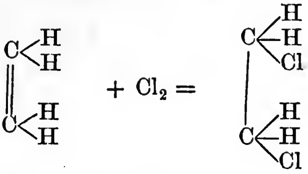
In the reactions of acetic acid, for example, the group C_2H_3O frequently passes unchanged as a radical into the new compound, and is then always monovalent. As the C_2 nucleus is hexavalent, the monovalent radical C_2H_3O must have the oxygen united to carbon with both its bonds.

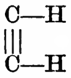
42. *Saturated and Unsaturated Organic Compounds.*—In cases where di- and trivalent union occurs between carbon atoms in organic compounds, these latter are frequently capable of uniting with further elementary atoms, especially so with the halogens and with nascent hydrogen, with change of the polyvalent union into monovalent.

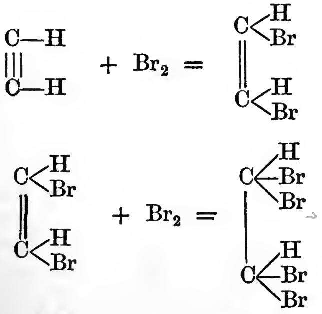
For example, the molecule of ethylene—



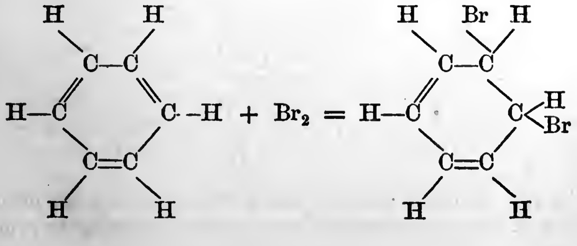
absorbs a molecule of chlorine (Cl_2), being thereby converted into an ethane derivative :



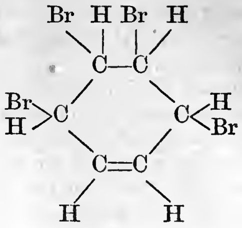
In the case of acetylene  the addition of halogen takes place in two stages :



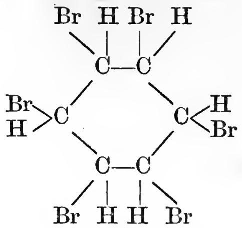
In benzene in three stages :



Benzene + $2Br_2$ =



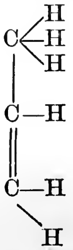
Benzene + $3Br_2$ =



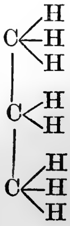
Compounds capable of union in this way are termed *unsaturated.*

When the capacity of saturation of a carbon nucleus is less than C_nH_{2n+2}, on account of its being closed in a ring form, the molecule acts as though saturated—i.e. cannot combine directly with halogens, nascent hydrogen, &c. In open chains the maximum capacity of saturation reachable is $2n + 2$, in single closed rings $= 2n$, in molecules with double rings $2n-2$, &c.

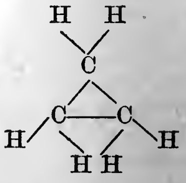
Whilst, for example, the molecule



is easily converted into



the nucleus valency increasing from $2n$, to $2n + 2$; by analogy, the body represented by the symbol



would not be easily affected, the nucleus valency remaining $2n$, as there is in it only monovalent carbon union, difficult to disjoin.

Isomerism.

43. In the foregoing paragraphs frequent mention has been made of compounds which, though possessing the same general molecular formulæ, exhibit different properties in consequence of the varying arrangements of their elementary atoms, being, in fact, different chemical bodies. Such compounds are termed *isomeric* (from ἰσομερής, composed of equal parts.) The term isomerism has in general a still further meaning, being applied to all bodies *which on ultimate analysis show the same percentage composition*—that is, contain the same elements in the same ratio. In consequence isomerism is divisible into several varieties.

44. *Polymerism.*—Bodies of the same percentage composition but of different molecular weight are termed polymeric compounds. Their molecular formulæ are either whole multiples of one another or at least of the same simplest atomic-ratio formula.

Such a difference has already been mentioned in § 22.

The simplest ratio formula	CH_2O
Corresponding body, acetic acid	$C_2H_4O_2$
Lactic acid	$C_3H_6O_3$
and grape sugar	$C_6H_{12}O_6$

Another group of polymeric bodies is formed by those hydrocarbons whose formulæ are multiples of CH_2.

Ethylene	C_2H_4	
Propylene	C_3H_6	
Butylene	C_4H_8	
Amylene	C_5H_{10}	
Hexylene	C_6H_{12}	&c.

These latter show considerable resemblance in their properties.

From this variety of polymerism, in which the difference is in the molecular weight only, there is distinguishable the further case of *genetic polymerism.* There is, namely, a pretty large number of organic bodies, which under certain circumstances are transformed directly into polymeric compounds of similiar chemical properties, in which several similar molecules have united to a single new one. Frequently this latter can be reconverted into the less complex original molecules by very simple means—for instance, by action of a high temperature.

Aldehyde, a liquid boiling at 21°, and which is miscible with water in every proportion, by contact with acids is converted into *paraldehyde,* boiling at 124°—and scarcely soluble in water; this latter, on superheating its vapour, is reconverted into aldehyde.

45. *Metamerism.*—In many cases of equal molecular weight and equal percentage composition, the respective compounds are decomposed into several organic bodies by reagents that are incapable of breaking the connection between the carbon atoms in the nuclei. Such compounds, therefore, contain several carbon nuclei united to one another by atoms of polyvalent elements, such as oxygen, sulphur, nitrogen, &c. In these cases the bodies are said to be *metameric.*

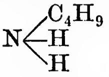
There are, e.g., three compounds of the molecular formula $C_3H_6O_2$, which yield, on treatment with caustic potash, salts of organic acids, propionic acid, methylic acetate, and ethylic formate. The reactions are expressed by the following equations :

$C_3H_6O_2$ Propionic acid.	$+$	KOH	$=$	$C_3H_5KO_2$ Potassic propionate.	$+$	HOH
$C_3H_6O_2$ Methylic acetate.	$+$	KOH	$=$	$C_2H_3KO_2$ Potassic acetate.	$+$	$CH_3.OH$ Methylic alcohol.
$C_3H_6O_2$ Ethylic formate.	$+$	KOH	$=$	$CHKO_2$ Potassic formate.	$+$	$C_2H_5.OH$ Ethylic alcohol.

giving for the three metameric bodies the formulæ—

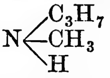
Propionic acid .	$H.O.C_3H_5O$
Methylic acetate .	$CH_3.O.C_2H_3O$
Ethylic formate .	$C_2H_5.O.CHO$

The following organic bases are also metameric :—



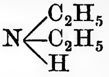
$N\begin{cases}C_4H_9\\H\\H\end{cases}$

Butylamine.



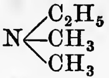
$N\begin{cases}C_3H_7\\CH_3\\H\end{cases}$

Propylmethylamine.



$N\begin{cases}C_2H_5\\C_2H_5\\H\end{cases}$

Diethylamine.

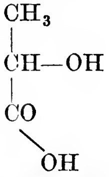


$N\begin{cases}C_2H_5\\CH_3\\CH_3\end{cases}$

Ethyldimethylamine.

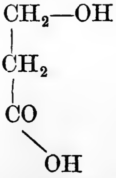
46. *Structural Isomerism.*—When the difference between several organic bodies of the same molecular formula is not due to metamerism, they are isomers in the strict sense of the word, *true isomers* or *structural isomers.* The organic radicals contained in them are of the same weight; the carbon nuclei contain the same number of atoms ; the difference in properties is caused by difference of position of points of attachment of other atoms to the nucleus (§ 39), or the difference of structure in nuclei of like number of carbon atoms.

As an instance of isomerism of the first kind—*place isomerism*—there may be mentioned, in addition to those given in § 39—



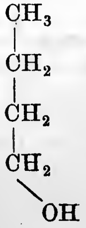
Fermentation lactic acid.

and

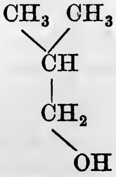


Ethylene lactic acid.

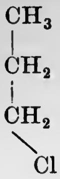
Of the many instances of isomerism of the second kind due to the method of mutual union of the carbon atoms, *nucleus isomerism*, there may be mentioned—



and



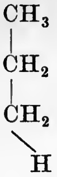
When in truly isomeric bodies the carbon is united to atoms of one monad element only, the isomerism must be due to nucleus isomerism. From the position isomeric bodies



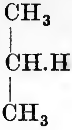
and

$CH_3-CH.Cl-CH_3$

there results, on replacement of the chlorine by hydrogen, identically the same hydrocarbon :

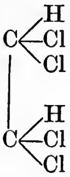


=

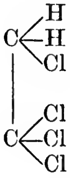


$CH_3-CH.H-CH_3$

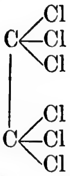
and on complete removal of all hydrogen atoms from the position isomers



and



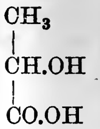
by chlorine there results the same chloride of carbon :



As our knowledge of the inner constitution of organic bodies is still in a great many cases very imperfect, and frequently entirely wanting, it results that for numerous undoubted cases of structural isomerism we are unable to settle to which kind it is due.

47. *Physical Isomerism.*—In a very few cases organic compounds of the same molecular formulæ, and possessing the same chemical properties, and in which any difference in structure is not only non-recognisable but highly improbable, exhibit differences in certain of their physical properties, more especially in their behaviour with polarised light. Such bodies are termed *physical isomers.*

One of the most striking instances of this kind of isomerism is given by ethylidene lactic acid :



$$\begin{array}{l} CH_3 \\ | \\ CH.OH \\ | \\ CO.OH \end{array}$$

which, prepared from the juice of flesh, rotates the plane of polarisation of a beam of polarised light, whilst that modification of the acid obtained by the fermentation of sugar is without any action on polarised light.

Very probably the reason of the difference between bodies only physically isomeric lies in an easily imaginable difference in the arrangement in space of atoms which are still united chemically in exactly the same way (geometric isomerism).

Homology and Homologous Series.

48. In opposition to the remarkable differences between organic bodies of like molecular formulæ, is the fact that bodies of different molecular composition frequently exhibit great similarity in all their chemical and physical properties.

The compounds in which these analogies are most marked are those whose formulæ differ by CH_2, or a whole multiple thereof, nCH_2, and whose molecular weights differ therefore by $\pm$ $14n$. It is of course obvious, from what has been said before, that a difference in composition of CH_2 does not make similar properties a necessary consequence; this only occurs when the respective substances agree with one another in their chemical constitution, their structure, and all essential points. This analogy of structure is especially shown in the fact that like reagents produce like changes, and further that the resulting products of such changes agree in properties, but differ in composition by CH_2. Such bodies are termed *homologous compounds*. They form members of a natural family of bodies which can be arranged according to their increasing contents of carbon. The similarity of physical properties between the members of a homologous series is greater the nearer they stand to one another on such a list—that is, the less they differ in chemical composition.

Such a homologous series is formed, for example, by

Methylic	alcohol	CH_4O
Ethylic	„	C_2H_6O
Propylic	„	C_3H_8O
Butylic	„	$C_4H_{10}O$
—	—	—
—	—	—
—	—	—
—	—	—
Cetylic	alcohol . . .	$C_{16}H_{34}O$
—	—	—
—	—	—
—	—	—
Mellissylic	alcohol . . .	$C_{30}H_{62}O$

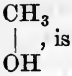
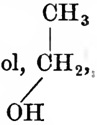
The members of this homologous series are all acted on in like manner by hydrochloric acid, yielding

$$\begin{array}{ll} CH_3Cl & \\ C_2H_5Cl & \\ C_3H_7Cl & \\ C_4H_9Cl & \&c. \end{array}$$

All members of a homologous series can be expressed by a single general formula—that for the above alcohols, e.g., is $C_nH_{2n+2}O$, or $C_nH_{2n+1}.OH$.

As the products of the same reaction also form a homologous series, the reaction may be represented by a general equation. The conversion of the alcohols into the corresponding series of chlorides is given by the single general equation:

$$C_nH_{2n+1}.OH + HCl = C_nH_{2n+1}Cl + H_2O.$$

49. The homology of organic bodies may be more or less complete; it is the more complete the larger the number of homologous products that can be obtained from them, and the more energetic the reactions producing such products. For example, methylic alcohol,  $\begin{matrix} CH_3 \\ | \\ OH \end{matrix}$, is as completely homologous as possible to ethylic alcohol,  $\begin{matrix} CH_3 \\ | \\ CH_2 \\ / \\ OH \end{matrix}$, or $CH_3.CH_2.OH$. Of the two propylic alcohols, on the other hand, one is so in less degree than the other; but both are acted upon in the above-mentioned way by the halogen acids:

$$\begin{array}{rl} & CH_3.OH + HCl = CH_3Cl + OH_2 \\ & CH_3.CH_2.OH + HCl = CH_3.CH_2.Cl + OH_2. \\ 1. & CH_3.CH_2.CH_2.OH + HCl = CH_3.CH_2.CH_2.Cl + OH_2. \\ 2. & CH_3.CH(OH).CH_3 + HCl = CH_3.CHCl.CH_3 + OH_2. \end{array}$$

Towards oxygen, however, their behaviour is essentially different. By the action of one atom of oxygen they all yield oxides of the general formula $C_nH_{2n}O$; but that from the first propylic alcohol only is really homologous to those from both the lower homologues:

$$\begin{array}{r} CH_3.OH + O = CH_2.O + OH_2 \\ CH_3.CH_2.OH + O = CH_3.CHO + OH_2 \\ CH_3.CH_2.CH_2.OH + O = CH_3.CH_2.CHO + OH_2, \end{array}$$

as these are all converted into homologous organic acids according to the general equation:

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

The oxidation product from the second propylic alcohol, $CH_3.CO.CH_3$, though containing CH_2 more than $CH_3.CHO$, still cannot unite simply with more oxygen, but on further oxidation takes up several oxygen atoms, with breaking up of the carbon nucleus.

Physical Properties of Organic Bodies.

Molecular and Atomic Volume.

50. The densities of organic bodies are the relative weights of equal volumes, at equal temperatures, expressed in abstract numbers; their specific gravities the weight of the volume unit of a cubic centimètre in grams. If the gram molecular weight of a body be divided by the specific gravity at a given temperature, the specific volume for that temperature—i.e. the volume in cubic centimètres of the molecular weight expressed in grams—is obtained. If the specific volumes be divested of their concrete significance, and conceived as abstract numbers only, they then form the relative molecular volumes. For example, the specific gravity at 0° of acetic acid is 1·075, its molecular weight = 60. Sixty grams of acetic acid at that temperature would therefore occupy a volume of 55·8 c.c.; this, then, is its specific volume. The specific volume of ethylic alcohol at 0° is similarly obtained as 57·05. Therefore the true molecules of acetic acid and of ethylic alcohol occupy at 0° spaces which are in the ratio of 55·8 : 57·1, these numbers forming the relative molecular volumes of the bodies.

51. Gases and vapours in the gaseous state contain, under like conditions of temperature and pressure, the same number of molecules in the same volume. Their specific and molecular volumes are, under the above conditions, equal to one another, whilst the specific gravities are directly as the molecular weights.

52. As fluids and solids do not expand equally for equal increments of temperature, they are not under like conditions of heat at equal temperatures; their specific and molecular volumes at like temperatures show no simple relation to one another. The molecular volumes of liquids near their boiling points, and of solids at their fusing points, show relations reducible to laws. These have been studied with more exactness in the case of liquids. If the molecular volumes of homologous compounds at their respective boiling points be compared with one another, there is found a difference proportional to that in the molecular weights, the molecular volume altering by about 22 for each alteration of the composition by CH_2 :

		Molecular Weight.	Molecular Volume.	Difference.
Formic acid . .	CH_2O_2	46	41·5	22
Acetic " . .	$C_2H_4O_2$	60	63·5	22
Propionic " . .	$C_3H_6O_2$	74	85·5	22
Butyric " . .	$C_4H_8O_2$	88	107·5	

In bodies which contain an equal number of atoms of oxygen, but differ in their composition by $(-C + H_2)_x$, the molecular volumes are equal:

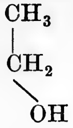
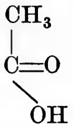
		Difference.	Molecular Volume.
Benzoic aldehyde .	C_7H_6O	$-C_2 + H_4$	118·5 (179° C.)
Valeral . .	$C_5H_{10}O$		118·8 (101° C.)

The increase in the molecular volume by the addition of two hydrogen atoms is therefore as great as the diminution produced by the removal of one carbon atom, or the change in molecular volume by an atom of carbon is twice as great as that produced by an atom of hydrogen. As the group CH_2 in homologous compounds alters the molecular volume by 22, the C and H_2 must have equal parts thereof—i.e. the alteration caused by a carbon atom = 11, by each hydrogen atom $^{11}/_2 = 5{\cdot}5$. These alteration values of the single elementary atoms are termed their *atomic volumes.*

Atomic volume C = 11.
Atomic volume H = 5·5.

The atomic volumes of other elements can be calculated in a similar manner.

An alcohol on conversion into an acid loses two hydrogen atoms, which are replaced by one oxygen atom, united by both its bonds to the same carbon atom. The alteration produced in molecular volume is very small, the mean result being + 1·2; e.g.

		Specific Volume.	Difference.
Ethylic alcohol		62·5 (78° C.)	1·2
Acetic acid		63·7 (118° C.)	

This gives as the molecular volume MV′ of a compound resulting from the replacement of 2H by O, from the change of the ingredients, $= \text{MV}' - 11 + 12{\cdot}2$.

The atomic volume, therefore, of oxygen when united to carbon by both its bonds = 12·2.

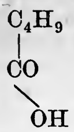
The molecular volume is not altered to the same amount by an oxygen atom, which is united by one of its bonds only to a carbon atom. From a variety of determinations the atomic volume of oxygen, when united in this way, is found to be about 6·4.

By analogous methods the following atomic volumes have been ascertained:—

Sulphur	united	by two bonds	to a carbon atom	= 28·6
”	”	one bond	”	= 22·6
Chlorine	”	” ”	”	= 22·8
Bromine	”	” ”	”	= 27·8
Iodine	”	” ”	”	= 37·5
Nitrogen	”	” ”	”	= 2·3
”	”	three bonds	”	= 28·0

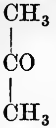
From these numbers the molecular volume of any organic compound can be calculated if the method of union of any oxygen, sulphur, or nitrogen atoms be known; e.g.

Molecular Volume.
Calculated. Found.



$$\begin{array}{l}C_4H_9\\ |\\ CO\\ \diagdown\\ \ \ OH\end{array} = 5 \times 11 + 10 \times 5{\cdot}5 + 12{\cdot}2 + 6{\cdot}4 = \quad 128{\cdot}6 \quad 130{\cdot}2$$

Valeric acid.



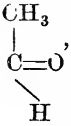
$$\begin{array}{l}CH_3\\ |\\ CO\\ |\\ CH_3\end{array} = 3 \times 11 + 6 \times 5{\cdot}5 + 12{\cdot}2 = \quad 78{\cdot}2 \quad 77{\cdot}6$$

Acetone.

$$\begin{array}{l}C_2H_5\\ |\\ O\\ |\\ C_2H_5\end{array} = 4 \times 11 + 10 \times 5{\cdot}5 + 6{\cdot}4 = \quad 105{\cdot}4 \quad 105{\cdot}6$$

Ethylic ether.

These results can also be applied in determining the method of union of the oxygen, sulphur, and nitrogen atoms in organic compounds.

If in the case of aldehyde, C_2H_4O, for instance, it were necessary to ascertain whether the formula should be written $C_2H_3.OH$ or  $\begin{array}{l}CH_3\\ |\\ C{=}O\\ \diagdown\\ \ H\end{array}$, the first would give as the molecular volume

$$2 \,.\, 11 + 4 \,.\, 5{\cdot}5 + 6{\cdot}4 = 50{\cdot}4,$$

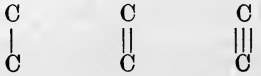
whilst the second would give

$$2 \,.\, 11 + 4 \,.\, 5{\cdot}5 + 12{\cdot}2 = 56{\cdot}2.$$

From the specific gravity of the body near its boiling point (21° C.) the molecular volume is found to be 56·45, showing the second formula to be correct.

It must be remarked, however, that the numbers calculated in the above way in many cases do not agree in a satisfactory manner with the molecular volumes derived from the found specific gravity. The values of the atomic volumes are still in part encumbered with considerable errors, and this must especially be the case with the atomic volume of carbon.

Just as an oxygen atom has a different atomic volume, when united by both bonds to the same atom, to that which it has when united by one bond only, so carbon may have different values according to whether it is united to another carbon atom by one, two, or three bonds.



$$\begin{array}{c}C\\ |\\ C\end{array} \qquad \begin{array}{c}C\\ \|\\ C\end{array} \qquad \begin{array}{c}C\\ |||\\ C\end{array}$$

The results of which the above is a summary were obtained at a time when the idea of a difference of the method of union of O, S, and N had already been partly evolved, but before any idea had been formed of the method of union of the carbon atoms. It is scarcely to be doubted that although a number of important points have been determined, still a repetition of the investigations, based on more complete recent theoretical views, would lead to very important modifications in our notions of atomic volumes.

The investigations of the molecular volume of solid organic bodies at analogous temperatures are not yet sufficiently complete to enable any laws to be deduced from them.

Melting Points and Boiling Points of Organic Bodies.

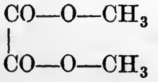
53. As melting and boiling points are amongst the characteristic properties of chemical bodies, they must be affected by the nature, number, and method of union of the elementary atoms forming the molecule. In what way these factors react upon the temperatures of fusion and ebullition is, however, not yet known, so that it is not possible to predict *à priori* these temperatures. Comparative investigations have, however, at least shown a few general laws, of which the following are the most important:—

54. *Melting Point.*—In homologous series the melting point frequently—but by no means invariably—increases with the molecular weight of the compound, without, however, these changes showing any complete parallelism with one another; e.g.

Series $C_nH_{2n+2}O$.			Series $C_nH_{2n}O_2$.			Melting Point.
			Caprylic acid		$C_8H_{16}O_2$	16°–17°
			Capric	,,	$C_{10}H_{20}O_2$	30°
			Lauric	,,	$C_{12}H_{24}O_2$	43·6°
			Myristic	,,	$C_{14}H_{28}O_2$	53·8°
Cetylic alcohol	$C_{16}H_{34}O$	50°	Palmitic	,,	$C_{16}H_{32}O_2$	62·0°
			Stearic	,,	$C_{18}H_{36}O_2$	69·2°
			Arachidic	,,	$C_{20}H_{40}O$	75°
Cerylic alcohol	$C_{27}H_{56}O$	78°	Cerotic	,,	$C_{27}H_{54}O_2$	79°
Myricylic ,,	$C_{30}H_{62}O$	88°	Mellissic	,,	$C_{30}H_{60}O_2$	88°

In many cases the group CH_3 exerts an influence in raising the melting point even where the CH_3 is united to the carbon nucleus by means of other elements, showing itself in opposition to the rule before mentioned of increase of molecular weight raising the melting point:

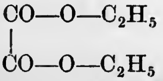
Methylic oxalate



$$\begin{array}{l} CO—O—CH_3 \\ | \\ CO—O—CH_3 \end{array}$$

m.p. 51°

Ethylic oxalate

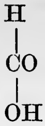


$$\begin{array}{l} CO—O—C_2H_5 \\ | \\ CO—O—C_2H_5 \end{array}$$

liquid.

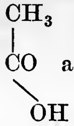
Similarly this influence is also perceived when the number of

CH_3 groups in direct union to the carbon nucleus is increased; for instance:

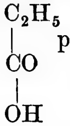


$H{-}CO{-}OH$

formic acid, m.p. 0°



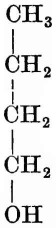
acetic acid, m.p. + 17°



$C_2H_5{-}CO{-}OH$

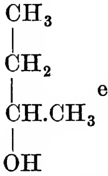
propionic acid, liquid below C. 0°

or still more strikingly by increase of methyl groups in certain cases of isomerism.



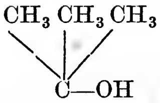
$CH_3{-}CH_2{-}CH_2{-}CH_2{-}OH$

propyl carbinol, liquid.



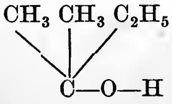
$CH_3{-}CH_2{-}CH.CH_3{-}OH$

ethyl-methyl carbinol, liquid.



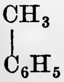
trimethyl carbinol, m.p. 25°.

On the other hand—



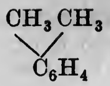
is liquid.

Similarly—

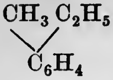


$CH_3{-}C_6H_5$

liquid.

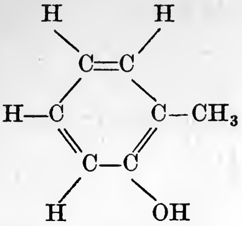


$\begin{array}{c} CH_3\ CH_3 \\ \diagdown\!\diagup \\ C_6H_4 \end{array}$ paraxylene, m.p. 15°.

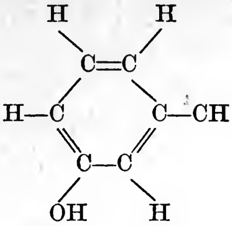


$\begin{array}{c} CH_3\ C_2H_5 \\ \diagdown\!\diagup \\ C_6H_4 \end{array}$ para-methyl-ethyl benzene, liquid.

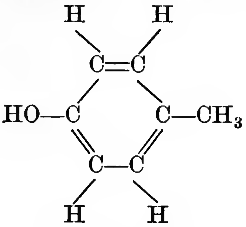
The melting point is influenced also by isomerism, due to the position of certain elements or groups on the nucleus, shown amongst other cases by



Ortho-cresol, liquid.

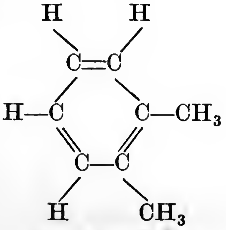


Meta-cresol, liquid.

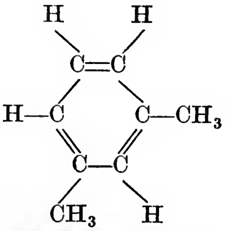


Para-cresol, m.p. 36°.

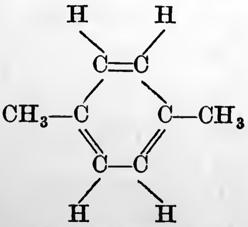
Quite analogously—



Ortho-xylene, liquid.



Meta-xylene, liquid.



Para-xylene, m.p. 15°.

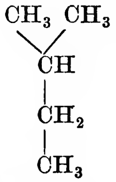
55. *Boiling Points.*—In homologous series the boiling points of the individual members mostly increase with the molecular weights, and in cases of complete homology (§ 49) very nearly proportionally to this increase in the molecular weight.

	Mol. Wt.	Boiling Point.	Difference. Mol. Wt.	Difference. Boiling Point.
Carbinol	CH_4O	60°	22	18·5°
Methyl carbinol . .	C_2H_6O	78·5°	22	19°
Ethyl carbinol . . .	C_3H_8O	97·5°	22	19·5°
a Propyl carbinol . .	$C_4H_{10}O$	117°	22	20°
a Butyl carbinol . . .	$C_5H_{12}O$	137°	22	20°
a Amyl carbinol . . .	$C_6H_{14}O$	157°		
Formic acid	CH_2O_2	99°	22	20°
Acetic acid.	$C_2H_4O_2$	119°	22	22°
Propionic acid. . . .	$C_3H_6O_2$	141°	22	21°
Normal buytric acid .	$C_4H_8O_2$	162°	22	22°
,, valeric acid . .	$C_5H_{10}O_2$	184°	22	21°
,, capric acid . .	$C_6H_{12}O_2$	205°	22	19°
,, œnanthylic acid	$C_7H_{14}O_2$	224°		

The view formerly held that the alteration of the molecular weight was completely proportional to that of the boiling point has not been corroborated by sufficient proof.

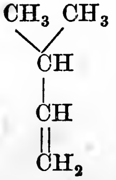
56. Of all the derivatives of a carbon nucleus the hydrogen compounds boil at the lowest temperature, the hydrogen atoms appearing to have a direct influence in lowering the boiling point; for it has been observed that in compounds of similar constitution in every respect but that one contains less hydrogen than the other, the one richest in hydrogen boils at the lowest temperature.

C_6H_{12}



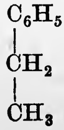
isopentane. Boils at 30°

C_6H_{10}



isoamylene. Boils at 35°

C_8H_{10}



$C_6H_5-CH_2-CH_3$

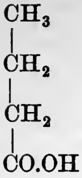
ethyl benzene. Boils at 134°

C_8H_8

$$\begin{array}{l} C_6H_5 \\ | \\ CH \\ \| \\ CH_2 \end{array}$$

Styrolene. Boils at 146°

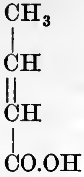
$C_4H_8O_2$



$$\begin{array}{l} CH_3 \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CO.OH \end{array}$$

Butyric acid. Boils at 162°

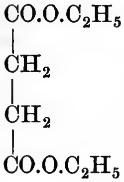
$C_4H_6O_2$



$$\begin{array}{l} CH_3 \\ | \\ CH \\ \| \\ CH \\ | \\ CO.OH \end{array}$$

Crotonic acid. Boils at 180°–182°

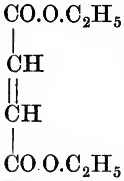
$C_8H_{14}O_4$



$$\begin{array}{l} CO.O.C_2H_5 \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CO.O.C_2H_5 \end{array}$$

Ethylic succinate. Boils at 217°

$C_8H_{12}O_2$



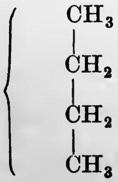
$$\begin{array}{l} CO.O.C_2H_5 \\ | \\ CH \\ \| \\ CH \\ | \\ CO.O.C_2H_5 \end{array}$$

Ethylic fumarate. Boils at 218°

&c.

57. Isomerism, due to the structure of bodies, exerts a very remarkable influence on the boiling point. It appears in cases of nucleus isomerism that the boiling point of the derivative of the normal carbon chains is always the highest, and that, in the fatty group of bodies, it sinks with the number of side chains, so that increase in the number of CH_3 groups exerts here exactly the opposite influence to that which it has on the melting point; for instance:

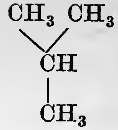
C_4H_{10}



$$\left\{ \begin{array}{l} CH_3 \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CH_3 \end{array} \right.$$

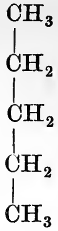
Butane. Boils at + 3°

C_4H_{10}



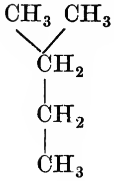
Isobutane. Boils at below 0°

C_5H_{12}

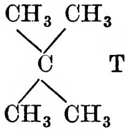


$$\begin{array}{l}CH_3\\ |\\ CH_2\\ |\\ CH_2\\ |\\ CH_2\\ |\\ CH_3\end{array}$$

Pentane. Boils at 39°

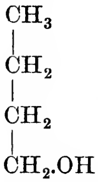


Isopentane. Boils at 30°



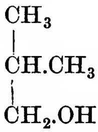
Tetra-methyl methane. Boils at + 9·5°

$C_4H_{10}O$



$$\begin{array}{l}CH_3\\ |\\ CH_2\\ |\\ CH_2\\ |\\ CH_2.OH\end{array}$$

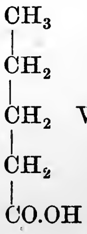
Propyl carbinol. Boils at 116°–117°



$$\begin{array}{l}CH_3\\ |\\ CH.CH_3\\ |\\ CH_2.OH\end{array}$$

Isopropyl carbinol. Boils at 106°–107°

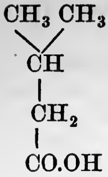
$C_5H_{10}O_2$



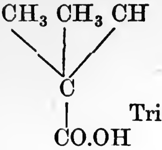
$$\begin{array}{l}CH_3\\ |\\ CH_2\\ |\\ CH_2\\ |\\ CH_2\\ |\\ CO.OH\end{array}$$

Valeric acid. Boils at 184°

$C_5H_{10}O_2$



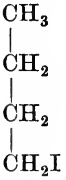
Isovaleric acid. Boils at 175°



Trimethyl acetic acid. Boils at 161°

If, in a hydrogenised organic body, hydrogen atoms are replaced by other elements, or by compound radicals, the boiling point is raised. If place isomerism can occur, the position of the substituted hydrogen atom will have a specific influence on the amount of increase. In the first substitution derivatives of the hydrocarbons, C_nH_{2n+2}, for example, the derivative of a terminal and primarily united carbon atom has always a higher boiling point than that of an intermediate secondarily united isomer of the same nucleus, and the boiling point of the place-isomeric tertiary products is still lower than this last.

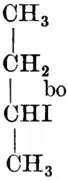
C_4H_9I:



$CH_3-CH_2-CH_2-CH_2I$

boils at 129°

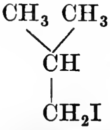
Primary.



$CH_3-CH_2-CHI-CH_3$

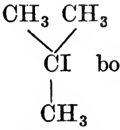
boils at 117°–118°

Secondary.



boils at 120·5°

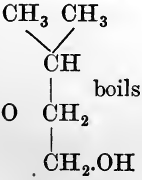
Primary.



boils at 99°

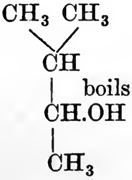
Tertiary.

$C_5H_{12}O$



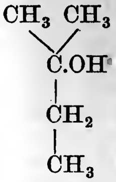
boils at 130°–131°

Primary.



boils at 106°–108°

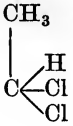
Secondary.



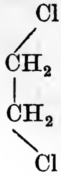
boils at 100°

Tertiary.

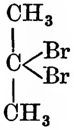
In place-isomeric, polysubstitution derivatives, the distance of the places exerts an essential influence :



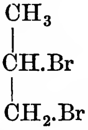
boils at 58°–59°



boils at 85°

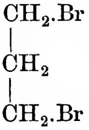


boils at 113°–116°



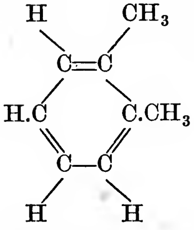
$CH_3-CH.Br-CH_2.Br$

boils at 142°

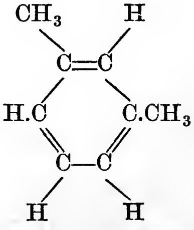


$CH_2.Br-CH_2-CH_2.Br$

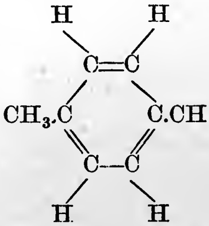
boils at 160°–163°



Orthoxylol, boils at 140°–141°.



Metaxylol, boils at 137°.



Paraxylol, boils at 136°.

Refraction of Light.

58. The quotient of the sine of the angle of incidence (i) of a beam of light of known wave-length passing from air into another transparent medium, divided by the sine of the angle of refraction (r), is the refractive index (n) of this latter medium, and as such is of constant value for each especial medium:

$$\frac{\sin i}{\sin r} = n$$

The value $\frac{n-1}{d}$, where d expresses the density of the respective medium, is termed the specific refractive power, and the product of the latter into the molecular weight P of the medium is termed the refraction-equivalent of the latter.

Sufficiently accurate estimations of this latter amount for a considerable number of pure organic compounds, selected however nearly entirely from the group of so-called fatty bodies, have shown some simple relations of it to the proportional composition, of which the most important will now be mentioned. The numerical values are for the line $\mu\ a$ of the spectrum from a Geissler's hydrogen tube.

1. The specific rotary powers of isomeric bodies are nearly equal to one another, therefore the refraction equivalents of polymeric bodies are nearly proportional to their molecular weights.

$$\text{Butyric acid } C_4H_8O_2,\ d = \cdot 961,\ n = 1\cdot 3955,\ \frac{n-1}{d} = \cdot 4116$$

$$\frac{n-1}{d}\,\text{P} = 36\cdot 62.$$

$$\text{Acetic aldehyde } C_2H_4O,\ d = \cdot 781,\ n\ 1\cdot 3298,\ \frac{n-1}{d} = \cdot 4222$$

$$\frac{n-1}{d}\,\text{P} - 18\cdot 58$$

but those of metameric and isomeric bodies are, on the contrary, of nearly equal amount; e.g.

$$\text{Butylic alcohol } C_4H_9.OH,\ d = \cdot 8074,\ n = 1\cdot 394,\ \frac{n-1}{d} = \cdot 4879$$

$$\frac{n-1}{d}\,\text{P} = 36\cdot 11$$

$$\text{Ethylic ether } C_2H_5.O.C_2H_5,\ d = \cdot 7166,\ n = 1\cdot 3511,\ \frac{n-1}{d} = \cdot 49$$

$$\frac{n-1}{d}\,\text{P} = 36\cdot 26$$

These simple values, however, invariably show certain deviations from perfect agreement, mostly too great to be explained as experimental errors. It therefore appears that the method of union of the elements in the compound, or chemical structure, has a measurable influence, whose nature has not yet been determined. The nature and mere number of the elementary atoms in the molecule is of more importance.

59. By comparison of the refraction equivalents of homologous organic compounds, it appears that they increase by a nearly equal amount for each addition of CH_2 to the molecule; e.g.

	d	n	$\frac{n-1}{d}$	$\frac{n-1}{d}P$	Difference.
$C_2H_4O_2$ acetic acid .	1·0514	1·3699	·3519	21·11	
$C_3H_6O_2$ propionic acid .	·9963	1·3846	·3860	28·57	7·46
$C_4H_8O_2$ butyric acid .	·9610	1·3955	·4116	36·22	7·65
$C_5H_{10}O_2$ valeric acid .	·9313	1·4022	·4319	44·05	7·83
$C_6H_{12}O_2$ caproic acid .	·9252	1·4116	·4449	51·61	7·56
$C_7H_{14}O_2$ œnanthylic acid	·9175	1·4192	·4569	59·40	7·79

60. By comparison of the refraction equivalents of bodies, which, whilst still having a similar molecular composition, differed only by having a different contents of the atoms of a single element, the proportion which the single elementary atoms have in that value has been approximately settled. For example, bodies containing the same number of oxygen and hydrogen atoms, but differing from each other by n carbon atoms, give a mean difference of $5\,n$, so that

the refraction equivalent of . $C = 5$
that of . . . . . $H = 1·3$
and that of . . . . $O = 3·00$

From these values the refraction equivalents of organic bodies can be calculated approximately; e.g.

Valeric acid $C_5 = 5 . 5 = 25$
$H_{10} = 10 . 1·3 = 13$
$O_2 = 2 . 3 = 6$

Total 44
Found 44·05

or

Propylic carbinol $C_4 = 4 . 5 = 20$
$H_{10} = 10 . 1·3 = 13$
$O = . 3 = 3$

Calculated 36
Found 36·11

As already mentioned, these laws at present have only been proved for bodies of generally analogous structure, such as the series of fatty acids and alcohols.

Optical Rotary Power.

61. Many organic compounds, mostly those physiologically resulting in the living organism, show the property, when in a liquid condition (or in solution), some even as vapour, of rotating the plane of polarisation of a beam of polarised light. Such bodies are termed optically active.

At constant temperature the degree of rotation of the polarised beam depends on the length of the layer of the active medium through which the ray has to pass (and on the amount of active substance if in solution). If the length of the layer be kept constant, and if no chemical change ensues on dilution, the amount of rotation is proportional to the concentration of the solution.

The *specific rotation*, or optical *rotary power*, is the angle (α) which is given by passage of a polarised ray through a layer one decimètre long of the rotary polarising substance (in the case of dissolved substances containing one gram of active substance in each c.c. of solution). This rotary power is one of the essentially constant properties of the respective organic substances.

The optical activity appears not to depend on the chemical structure, as active bodies are converted into inactive isomeric modifications without change of structure or of essential chemical properties. Very frequently this change ensues on mere warming. The reason of this different behaviour of optically isomeric organic bodies of similar structure is still unexplained, but may be due to a different arrangement of the atoms in space, the actual connection between the atoms still being the same.

Action of High Temperature on Organic Compounds.

62. All carbon compounds suffer chemical change when heated to sufficiently high temperature. This latter depends on the number, nature, and grouping of the elementary atoms in the molecule, and differs greatly with different bodies. Solid or liquid bodies which cannot be distilled unchanged, only require to be heated in distillation vessels, which prevent the access of oxygen; bodies which volatilise unchanged, require to be heated to temperatures above their boiling points. This is best effected by passing their vapours through glowing tubes, the greatest possible contact between the walls of the tube and the vapour being obtained. The process of chemical change effected by strong heating, the dissociation of organic bodies, is termed *dry distillation.* It depends on the general action of high temperatures in weakening or destroying the chemical affinities which have held the atoms together, so that decompositions ensue, accompanied by the formation of new bodies more stable at high temperatures.

In many cases the decomposition is of very simple nature, and, as a rule, then occurs with elimination of water, or carbonic anhydride, or both; e.g.

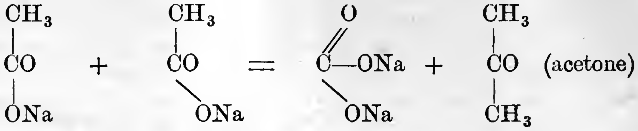
Malic acid at 200°, $C_4H_6O_5 = H_2O + C_4H_4O_4$
(Maleic and fumaric acids.

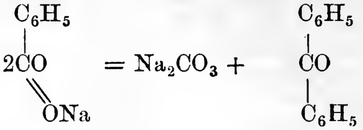
Citric acid at 175°, $C_6H_8O_7 = H_2O + C_6H_6O_6$
(Aconitic acid.)

At higher temperatures aconitic acid $C_6H_6O_6 = CO_2 + C_5H_6O_4$
(Itaconic and citraconic acids.)

„ „ „ tartaric acid $C_4H_6O_6 = CO_2 + H_2O + C_3H_4O_3$
(Pyrotartaric acid.)

Products of simpler composition are not invariably formed. Frequently at the moment of decomposition several nuclei unite together to form more complex products, as, for instance, in the dry distillation of salts of organic acids, where, especially in the case of alkaline and alkaline earthy salts, a carbonate is left, whilst the remaining nuclei of two original molecules unite to form a new compound, e.g. sodic acetate:




(Sodic benzoate.) (Benzophenone.)

63. Not seldom these processes occur without formation of essential quantities of bye-products, but mostly, especially in the dry distillation of complex bodies, the number of products is very large, and includes bodies of both greater and less complexity. The distillation products of the same body differ essentially in nature, quantity, and state of aggregation according to the temperature at which decomposition is effected.

In the dry distillation of wood, which has the formula $C_6H_{10}O_5$, or more probably some multiple, there are first given off gases and an aqueous liquid. The first contains much CO_2, later follow carbon monoxide, then gaseous hydrocarbons, such as CH_4, C_2H_4, C_2H_2, &c., and on very strongly heating, hydrogen also. Water at first passes over in largest quantity, but is soon followed by acetic acid, $C_2H_4O_2$, wood spirit, CH_4O, acetone, C_3H_6O, &c., which remain dissolved in the former. When the oxygen of the wood has been in great part removed in the form of these and similar highly oxygenated compounds, there follow (generally at the same time as the gaseous hydrocarbons) more difficultly vapourisable compounds, poorer in oxygen, and of more complex constitution, such as phenol C_6H_6O, cresol C_7H_8O, &c., as also hydrocarbons of higher molecular weight, e.g. benzol C_6H_6, naphthalene $C_{10}H_8$, anthracene $C_{14}H_{10}$, &c. These all condense in cooled receivers, and form two layers, an aqueous and an oily. The latter is nearly invariably of a dark colour, and consists of solutions of solid bodies in oily products, and often mixed with bodies still solid. This layer is termed *tar*. From tar the various constituents which boil at different temperatures can be generally separated by fractional distillation. As a rule, those bodies which are liquid at ordinary temperatures distil sooner than solids. If the first are distilled off, a brownish black resinous mass, termed *pitch*, is left.

In the original distillation vessel a residue of charcoal is left, still containing all the mineral constituents of the original substance, which are left as ash on complete combustion. In the dry distillation of nitrogenous bodies, much ammonia is evolved, and is found as carbonate in the aqueous distillate, whilst the tar then invariably contains nitrogenous liquid bases, such as aniline, pyridine, &c., and the residual charcoal still contains some nitrogen, which cannot be separated from the carbon even at a white heat.

Putrefaction, Decay, and Fermentation of Organic Bodies.

64. If organic bodies are left in a damp condition at ordinary temperatures, many of them suffer apparently completely spontaneous changes, whose products show some similarity to those of dry decomposition. There are formed, namely, in addition to gases and volatile bodies, frequently of unpleasant odour (odour of putrefaction), also aqueous and even oily products and tarlike masses, or at least a dark-coloured residue, rich in carbon (humus). In general, the resemblance of these products to those of dry distillation, are the closer, the more completely oxygen has been excluded during their formation.

These changes are, however, in all probability never entirely spontaneous. To their initiation an exposure, however short, to air is essential; they are prevented by high or very low temperatures, by absence of water, and by the presence of certain poisonous bodies—antiseptic media. Amongst these latter are arsenious acid, mercury and zinc salts, tannin, creosote, and also common salt in concentrated solution.

65. During the exposure of putrescible bodies to air, they come in contact with the germs of microscopic organised beings, which by their evolution and multiplication are the primary cause of decomposition. As their vegetation occurs most vigorously at temperatures of 20°–30°, they most readily cause decomposition at these temperatures. Below 0° these beings lose the power of growth for at least the time of duration of that temperature. At temperatures near the boiling point of water they are killed like all other organisms, as also by antiseptic poisons.

66. Putrefaction and decay cannot be sharply separated from one another; by the first term are meant those decomposition processes which occur under the aid of organisms, and without action of oxygen, whilst in decay intense oxidising action occurs at the expense of the atmospheric oxygen.

To putrescible bodies especially belong the nitrogenous and sulphuretted constituents of animals and plants, the albuminoïd bodies or proteïd substances: e.g. albumen, caseïn, the substance of muscle and membrane, &c.

67. A very minute amount of the above-mentioned putrefaction-excitants can cause the decomposition of very considerable quantities of decomposable bodies, the latter probably serving as the nutritive material for many quickly following generations of the first. The decomposition products must then be considered as the excreta of these organisms. Such reactions as these are termed fermentations, and the bodies causing the change, whilst they themselves apparently take no visible part, are termed *ferments.*

68. One and the same body may undergo very different decompositions, according to the nature of the ferment acting on it, or according to the variations in the growth of the ferment produced by temperature, amount of moisture, &c.

Cane sugar, e.g., in contact with many organised ferments, is converted—with combination of the elements of water—into glucose:

$$\underset{\text{(Cane sugar.)}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{(Glucose.)}}{2C_6H_{12}O_6};$$

whilst the solution of the latter is converted by the ferment of putrid proteïd bodies into lactic acid:

$$C_6H_{12}O_6 = 2C_3H_6O_3 \text{ (lactic acid),}$$

which is further converted into butyric acid, with evolution of carbonic anhydride and hydrogen:

$$2C_3H_6O_3 = \underset{\text{(Butyric acid.)}}{C_4H_8O_2} + 2\,CO_2 + 2H_2.$$

If any unaltered glucose be present during this latter fermentation it is converted into mannite:

$$C_6H_{12}O_6 + 2H = C_6H_{14}O_6 \text{ (mannite).}$$

These and similar fermentations occurring without direct participation of atmospheric oxygen, may be considered as putrefactive processes, as also the decomposition of glucose into carbonic anhydride and alcohol under the influence of yeast:

$$C_6H_{12}O_6 = 2CO_2 + 2C_2H_6O \text{ (alcohol).}$$

In other fermentations the atmospheric oxygen is actively engaged, as in the acetic fermentation of alcohol:

$$C_2H_6O + O_2 = H_2O + C_2H_4O_2 \text{ (acetic acid).}$$

These, however, more closely resemble the decay processes of complex albuminoïd bodies.

69. As already mentioned, the ferments are frequently organised, often single cells of plant-like nature, sometimes also having the power of motion, as in the butyric ferment. There are also some ferments which are not organised, such as synaptase and diastase; these are soluble in water, and under favourable circumstances can cause large quantities of certain other compounds to suffer specific changes.

The amygdalin of bitter almonds in presence of water is decomposed, by the synaptase contained in the same seeds, into bitter almond oil, glucose, and hydrocyanic acid:

$$\underset{\text{(Amygdaline.)}}{C_{20}H_{27}NO_{11}} + 2H_2O = CNH + 2C_6H_{12}O_6 + C_7H_6O.$$

No other ferment is capable of producing this decomposition.

Not seldom inorganic compounds can act on organic bodies in a ferment-like manner, especially strong acids and sometimes strong basic hydrates.

70. By processes of putrefaction, decay, and fermentation, animals and plants gradually vanish after death, only the non-volatile mineral constituents remaining behind. By long-continued addition of oxygen they are converted into volatile products, especially into carbonic anhydride, water, and ammonia, which then serve anew as nourishment to the vegetable world.

It is often of great economical importance to preserve unchanged the very putrescible nitrogenous foods. This may be effected either by placing them under conditions under which fermentation is impossible, even in the presence of ferments, as, for instance, by freezing, or by destroying all ferments present.

By bringing bodies capable of putrefying into contact with salt, sugar, alcohol, or similar media, the water necessary for fermentation is removed, and they therefore remain unchanged. The same result is arrived at by drying at high temperatures. By smoking another result is obtained in addition to drying, the substances getting saturated with creosote, volatile oils, &c., which kill the organisms causing putrefaction.

The conservation of foods by Appert's method, which consists in heating them in tins to the temperature of boiling water, and then hermetically closing the latter whilst still at that temperature, depends on the destruction of all putrefactives at the boiling heat. So long as no air can reach the food to convey fresh germs to it, it remains unaltered at ordinary temperatures; from the moment of contact with air putrefactive action starts, which can be again destroyed by heating to boiling.

In order to preserve anatomical preparations, they are treated with solutions of mercuric chloride, zincic chloride, arsenious acid, &c.

The chief mass of wood, the cell substance, is not capable of putrefaction, but from the presence of albuminous substances in the wood, which can go into putrefaction under favourable conditions, the woody fibre is often destroyed. This is prevented either by washing the putrescible substances out of the wood (by steaming under pressure), or by forcing substances into it which prevent putrefaction (antiseptic media). The wood is saturated with cupric sulphate or corrosive sublimate solutions, or with 'pyrolignate of iron,' in which latter case the presence of creosote is especially active.

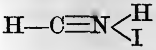
CYANOGEN COMPOUNDS.

71. By the name cyanogen the group CN ($=$ Cy) is understood, which acts generally as a monovalent radical. It can exist in several modifications, accordingly as the combining metal is united to the carbon or to the nitrogen atom.

In the first case, the two elements are united to each other by three bonds:

$$\begin{array}{l} C\equiv N \\ | \\ R \end{array}$$

In that case the radical is termed *true cyanogen* (generally *cyanogen* only) or *carbonitrile*, and, similarly to ammonia, possesses the power, after the saturation of the fourth carbon bond, of forming further and less stable compounds:



$$H{-}C{\equiv}N{<}^{H}_{I}$$

In the second modification of cyanogen, *Isocyanogen* or *Carbammonium*, both elements appear to be in tetravalent union, so that the nitrogen becomes the grouping element:

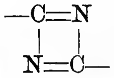
$$C\underline{\equiv}N{-}R.$$

Finally, there is a third modification, *Pseudocyanogen*, in which the C and N are in divalent union, as in the case of certain cyanates, for example:

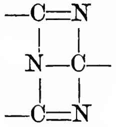
$$K{-}N{=}C{=}O$$

72. Cyanogen compounds are in the highest degree capable of polymerisation. That the reason of this property lies in the cyanogen group itself is indubitable; still the manner in which several such groups unite to a single radical is not yet determined with certainty. The following formulæ possess probability, and are not in contradiction with any known facts. In them, as in carbonitrile, every carbon atom is united by three bonds to nitrogen atoms, every nitrogen by three bonds to carbon, and the combination to other elements is effected through the carbon atoms:

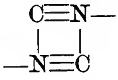
Dicyanogen (divalent)



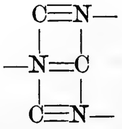
Tricyanogen (trivalent)



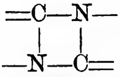
Similarly for the isocyanogen groups:



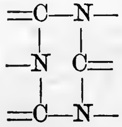
and



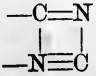
and for the pseudocyanogen groups:

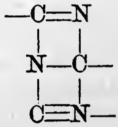


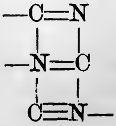
and



and even for polycyanogens in which the combination is a mixture of the two first:







73. *Formation of Cyanogen Compounds.*—The methods of formation of cyanogen compounds by the simultaneous decomposition of carbonaceous and nitrogenous compounds are pretty numerous, and will be spoken of hereafter. Of more immediate interest is the formation of the cyanogen group, either from its elements, or from their mineral compounds. Although carbon and nitrogen will not unite with one another directly, yet in the presence of strongly positive metals they combine and form the respective cyanides. If, for instance, potassium and carbon are mixed, and the mixture heated in an atmosphere of nitrogen, potassic cyanide is obtained :

$$K_2 + 2C + N_2 = 2KCN.$$

Instead of employing the free metal, a combination of the method of obtaining it from its carbonate with the method for preparing the cyanide can be used : a mixture of potassic carbonate is heated with excess of carbon in an atmosphere of nitrogen :

$$K_2CO_3 + 4C + N_2 = 3CO + 2KCN.$$

It is still more usual to employ the nitrogen in form of some of its compounds—ammonia or its salts, for instance—but best of all in the form of nitrogenous animal charcoal, and to heat the latter with potassic carbonate. Also by passing ammonia gas over ignited charcoal, a cyanogen compound—ammonic cyanide—is obtained :

$$C + 2NH_3 = NH_4.CN + H_2.$$

The crude material for the preparation of most cyanogen compounds is potassic cyanide, prepared by one of the above methods, which, for convenience in purification, is next converted into potassic ferrocyanide—yellow prussiate—K_4FeCy_6.

74. *Hydrocyanic Acid, or Prussic Acid.*

$$HCy = H—C\equiv N.$$

Hydrocyanic acid is readily obtained from parts of certain plants, as bitter almonds, kernels of stone fruits, leaves of cherry, laurel, &c., when they are left for some time at the ordinary temperature in a moist and finely divided state. The respective parts of these plants contain a bitter-tasting, crystallisable organic substance, amygdalin, together with an albuminoid body, synaptase or emulsine, which, acting as a ferment on the amygdalin, causes its decomposition; with addition of the elements of water, the amygdalin is converted into hydrocyanic acid, sugar, and bitter almond oil :

$$C_{20}H_{27}NO_{11} + 2H_2O = CNH + 2C_6H_{12}O_6 + C_7H_6O.$$

In the pure state, hydrocyanic acid is prepared by heating metallic cyanides with strong acids :

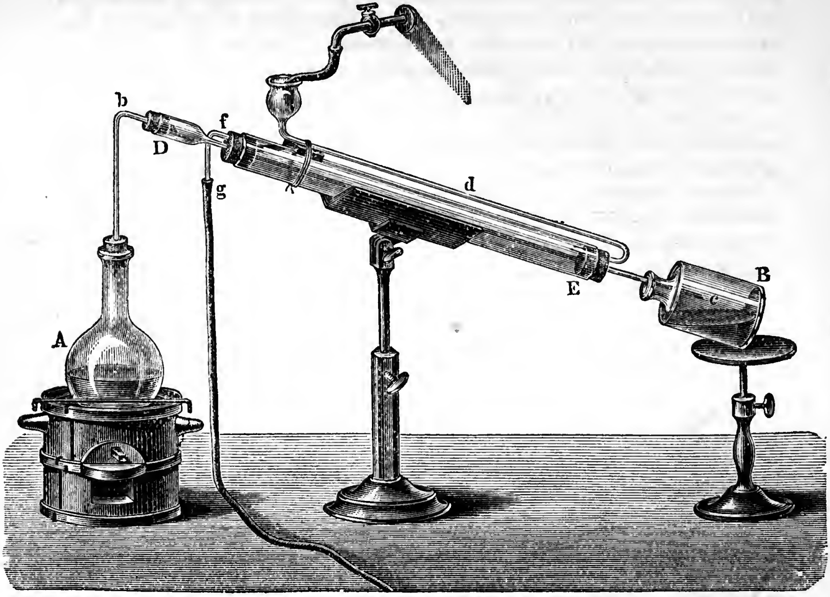
$$KCN + HCl = HCN + KCl.$$

Usually it is prepared from potassic ferrocyanide. Ten parts of this salt are treated with a mixture of six parts of concentrated sulphuric acid and forty parts of water in a flask (fig. 16, A), connected, by means of the bent tube *b*, with the condensing apparatus D E. The flask is heated until the liquid begins to boil, and the distillate is collected in the receiver B.

There is thus obtained an aqueous prussic acid, which readily decomposes on keeping; the addition of a drop of sulphuric acid renders it much more stable.

By the action of sulphuric acid upon potassic ferrocyanide, only one-half of its cyanogen is evolved as hydrocyanic acid, there being formed at the same time a white insoluble cyanide of iron and potassium of the formula $K_2Fe_2C_6N_6$, which is not attacked by dilute sulphuric acid. The reaction taking place is represented by the equation:

Fig. 16.



$$2K_4Fe(C_6N_6) + 3H_2SO_4 = 3K_2SO_4 + 6HCN + K_2Fe_2(C_6N_6).$$

From the aqueous hydrocyanic acid, the anhydrous acid can be obtained by fractional distillation, and treatment with calcic chloride; the pretty concentrated aqueous solution is slightly warmed, and the vapour of the easily volatile acid condensed in a receiver cooled by means of ice, and containing fused calcic chloride in coarse powder. The receiver is tightly stoppered, and allowed to stand till the salt has united to all the water; then, by application of gentle heat, the anhydrous acid is distilled, and collected in a receiver cooled by a freezing mixture of ice and salt.

75. Hydrocyanic acid is a colourless, mobile liquid, solidifying at 15° to a fibrous crystalline mass, and boiling at + 26·5°. In consequence it evaporates with extraordinary rapidity, and thereby absorbs so much heat that a drop placed on a glass rod can be caused to partly solidify by being moved quickly through the air. The density of the liquid is ·7058 at + 7° and ·6969 at + 18°, vapour density ·948. The odour is peculiar, somewhat resembling that of bitter almonds; the vapour of the acid burns with a pale violet-coloured flame.

The extraordinarily poisonous nature of hydrocyanic acid is especially noticeable. When mixed with much air, and inhaled in small quantity, it produces a peculiar feeling in the throat; in larger quantity, faintness, and finally death. The unmixed vapour of the anhydrous acid causes instant death, and produces equally fatal results by direct contact with the blood. In very small doses it is employed as a medicine. The acid character of HCN is not strongly pronounced; litmus paper is scarcely reddened by it; with metallic oxides, however, it behaves similarly to the halogen hydroacids, yielding generally metallic cyanides and water. When added to the oxides of iron it readily forms ferric ferrocyanide or Prussian blue, from which substance it derives its common name of prussic acid.

This formation of Prussian blue serves for the detection of small traces of cyanogen compounds. Usually the liquid to be tested is mixed with a ferrous salt, slight excess of KHO added, and the liquid heated for a short time. According to the equations:

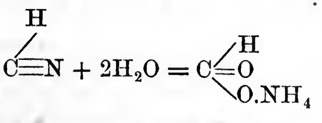
$$6HCN + FeSO_4 + 8KOH = 6KCN + Fe(OH)_2 + K_2SO_4 + 6OH_2$$

and

$$6KCN + Fe(OH)_2 = K_4FeC_6N_6 + 2KOH$$

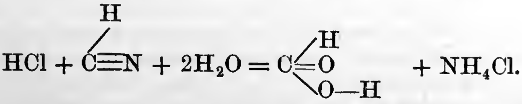
potassic ferrocyanide is formed; on then adding ferric chloride and acidulating with hydrochloric acid, a deep blue precipitate is obtained.

76. By keeping, hydrocyanic acid soon decomposes, brown solid bodies separating, and ammonic salts being formed. As already mentioned, a trace of a strong acid retards this decomposition, as does also dilution with large quantities of water. The aqueous solution forms by its decomposition some quantity of ammonic formate:



$$\overset{H}{C}\equiv N + 2H_2O = C\begin{cases}H\\ =O\\ O.NH_4\end{cases}$$

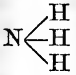
By boiling with alkalies this change is considerably accelerated, as also by heating with strong mineral acids; hydrochloric acid, for instance, decomposing hydrocyanic acid into ammonic chloride and formic acid:



$$HCl + \overset{H}{C}\equiv N + 2H_2O = C\begin{cases}H\\ =O\\ O-H\end{cases} + NH_4Cl.$$

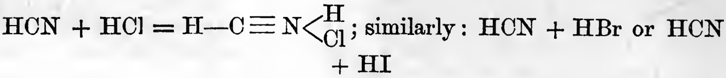
This easy conversion of the cyanogen into the oxatyl group CO.OH is highly characteristic of the 'true' cyanogen compounds, and is of great importance in organic synthesis

77. *Addition Products of Hydrocyanic Acid.*—As already mentioned, in certain respects hydrocyanic acid shows properties which place it amongst the analogues of ammonia. It may therefore be viewed as a molecule of ammonia, in which the three hydrogen atoms have been replaced by the trivalent radical formyl CH.



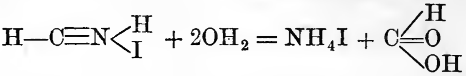
$$N\equiv(C-H).$$

In the anhydrous state it yields white crystalline compounds by direct union with HCl, HBr, or HI:



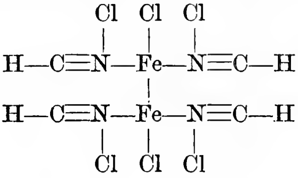
$$HCN + HCl = H-C\equiv N\lt\begin{matrix}H\\Cl\end{matrix};\ \text{similarly: } HCN + HBr \text{ or } HCN + HI$$

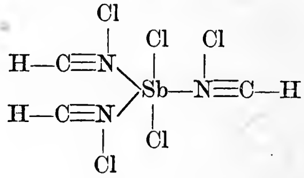
These compounds are decomposed with great rapidity, on treatment with water, into formic acid and ammonic salts:



$$H-C\equiv N\lt\begin{matrix}H\\I\end{matrix} + 2OH_2 = NH_4I + C\begin{matrix}\diagup H\\ =O\\ \diagdown OH\end{matrix}$$

Anhydrous hydrocyanic acid also unites with some metallic chlorides, crystalline compounds resulting; for instance, $Fe_2Cl_6,4HCN$ and $SbCl_5,3HCN$, the constitution of these bodies being probably





Metallic Compounds of Cyanogen.

78. The metallic cyanides can be prepared, almost without exception, from hydrocyanic acid, though only in the case of the most strongly positive metals, by action in the metallic state upon the acid:

$$K_2 + 2HCN = 2KCN + H_2;$$

yet by use of the hydrates, in some cases also of the oxides, they can be prepared without difficulty:

$$HgO + 2HCN = Hg(CN)_2 + H_2O.$$

The insoluble metallic cyanides are best prepared by double decomposition between the soluble alkaline cyanides, and soluble salts of the respective metals.

The cyanides of the different metallic groups differ from one another very essentially in some of their properties. Whilst those of the most positive metals (the alkalies and alkaline earths) are easily soluble in water, are of strongly alkaline reaction, are decomposed by the weakest mineral acids, even carbonic, and are not decomposed by a red heat if air be absent; those of the less positive metals (the heavy metals) are mostly insoluble, or difficultly soluble in water, and are decomposed by a high temperature. Some of these latter cyanides, more especially those of the noble metals (mercury, silver, &c., partly also Cu and Zn), simply decompose into the metal and cyanogen, which in great part comes off as gas, whilst the others, especially those of the iron group, are decomposed on ignition, nitrogen being evolved, and a compound of the metal with carbon left behind.

The cyanides of the heavy metals mostly combine with those of the alkalies, forming compounds soluble in water. In these double cyanides very frequently the less positive heavy metal is apparently more firmly united than the more positive, and cannot be recognised by its usual tests; when treated with mineral acids these compounds yield no hydrocyanic acid, or give up their cyanogen only partially in that form, whilst hydric metallic cyanides of acid character result; e.g. potassic ferrocyanide yields, with hydrochloric acid, potassic chloride and hydroferrocyanic acid:

$$K_4FeC_6N_6 + 4HCl = 4KCl + H_4FeC_6N_6.$$

In such double cyanides heavy metals can replace the alkali metal, and such replacing metals are still recognisable by their ordinary reagents.

These double cyanides can only result from the polymerisation of the cyanogen group, in some the dicyanogen, in others the tricyanogen group occurring.

Some metallic cyanides doubtless contain true cyanogen—that is, the metal united to carbon—whilst others appear to be entirely isocyanides; to the latter class probably belong the cyanides of those metals which combine readily with nitrogen, especially those which yield amid-compounds with ammonia.

79. *Potassic Cyanide*, KCy or $K—C\equiv N$.—Although potassic cyanide can be directly prepared, still it is generally obtained from dried potassic ferrocyanide, which is heated to quiet fusion, without access of air:

$$K_4FeC_6N_6 = 4KCN + FeC_2 + N_2.$$

The carbide of iron settles to the bottom, and the clear supernatant liquid can be poured off. Such potassic cyanide as remains with the residue can be obtained by pulverisation and extraction with boiling alcohol; the filtered liquid crystallises on cooling.

It can be obtained in larger quantity, and of sufficient purity for most purposes, by heating a mixture of eight parts of dried potassic ferrocyanide with three parts of dried potassic carbonate to low redness in an iron crucible. By this means one-half of the cyanogen, which would be lost but for the addition of the potash, is obtained as potassic cyanide, the other half as potassic cyanate, which latter remains mixed with the cyanide; instead of ferric carbide, spongy iron results, from which the melted salt is easily separated mechanically:

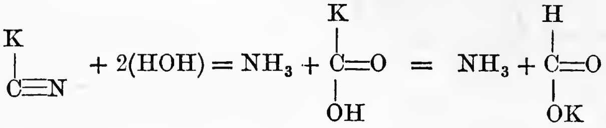
$$K_4Fe(C_6N_6) + K_2CO_3 = 5K(CN) + KCNO + CO_2 + Fe.$$

A still better result is obtained when charcoal is also added to the fusion, and the mixture strongly heated, the carbon reducing a large quantity of cyanate to cyanide of potassium :

$$K_4Fe(C_6N_6) + K_2CO_3 + C = 6K(CN) + CO_2 + CO + Fe.$$

The purest potassic cyanide is obtained by passing the vapour of anhydrous hydrocyanic acid into a solution of potassic hydrate in absolute alcohol, the salt separating in the crystalline form.

Potassic cyanide is a colourless, highly poisonous body, crystallising from solution in octahedra, from fusion in cubes; at a red heat it fuses to a clear liquid, it deliquesces in damp air, and—through its slow decomposition by the carbonic acid of the air—smells of hydrocyanic acid. Its aqueous solution reacts strongly alkaline. It is more soluble in dilute than in strong alcohol. It decomposes easily in aqueous solution, especially on boiling, into potassic formate and ammonia :



$$\begin{array}{c}K\\|\\C\equiv N\end{array} + 2(HOH) = NH_3 + \begin{array}{c}K\\|\\C=O\\|\\OH\end{array} = NH_3 + \begin{array}{c}H\\|\\C=O\\|\\OK\end{array}$$

When fused in contact with air, it absorbs oxygen, and is converted into cyanate. It undergoes the same change when heated with metallic oxides, and is therefore one of the most powerful reducing agents, e.g.

$$SO_2 + 2KCN = S + 2KCNO.$$

The cyanides of the other alkali metals resemble that of potassium in nearly all particulars.

80. *Ammonic cyanide*, $CN_2H_4 =$  $\begin{array}{c}C\equiv N\\|\\NH_4\end{array}$, is usually prepared by heating an intimate mixture of potassic cyanide and sal ammoniac. It crystallises in colourless cubes, which are very soluble in alcohol. It boils at + 36° with dissociation into hydrocyanic acid and ammonia, which re-combine on reduction of temperature. It is as poisonous as prussic acid and potassic cyanide. On keeping, it decomposes, with formation of a blackish brown mass (azulmine).

The formation of ammonic cyanide by passing ammonia gas over glowing carbon :

$$3C + 4NH_3 = 2(CN.NH_4) + CH_4;$$

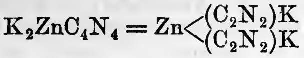
or by passing ammonia and carbonic oxide through red-hot tubes :

$$CO + 2NH_3 = CN.NH_4 + H_2O;$$

is of considerable theoretical interest. As ammonic cyanide is obtained by the destructive distillation of nitrogenous organic bodies, it occurs, often in considerable quantity, as a constituent of the wash-water of gas-works.

81. *Cyanides of the alkaline earths*—i.e. of barium, strontium, and calcium—can be prepared directly, but are best obtained by ignition of the respective ferrocyanides, or by action of hydrocyanic acid on their hydrates. They are more difficultly soluble than the foregoing, react alkaline, and are very easily decomposed by carbonic acid.

82. *Zincic cyanide*, $ZnC_2N_2 = Zn(CN)_2$, is obtained as a white insoluble powder, by addition of hydrocyanic acid to zincic acetate, or of potassic cyanide to any other zinc salt. It is decomposed by acids with evolution of hydrocyanic acid, is readily soluble in excess of potassic cyanide, the solution yielding on evaporation octahedral crystals of *potassic zincic cyanide*:

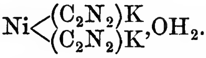


$$K_2ZnC_4N_4 = Zn{<}\begin{matrix}(C_2N_2)K\\(C_2N_2)K\end{matrix}$$

The cyanogen compounds of cadmium and indium are quite similar; from the double cyanides the metals are precipitated by sulphuretted hydrogen, as in the case of the ordinary salts.

Indium cyanide, however, is distinguished from the others by its easy decomposition on boiling with water, indium hydrate being formed:

$$In(CN)_2 + 2H_2O = In(OH)_2 + 2HCN.$$

83. *Nickelous cyanide*, $Ni(CN)_2$, is obtained similarly to the zinc salt, as an apple-green precipitate; it is easily dissolved by an aqueous solution of potassic cyanide to a yellow solution, which by evaporation yields monoclinic prisms of *potassic nickelous cyanide*, $K_2NiC_4N_4,OH_2$ or  $Ni{<}\begin{matrix}(C_2N_2)K\\(C_2N_2)K\end{matrix},OH_2$. From solutions of this salt, nickelous cyanide is re-precipitated by careful addition of hydrochloric acid; excess of acid decomposes it. By boiling the solution with mercuric oxide, nickelous oxide is precipitated, and potassic mercuric cyanide formed.

84. *Cyanides of Cobalt.*—By careful addition of potassic cyanide to a cobaltous salt, a reddish-brown precipitate of cobaltous cyanide is obtained, which dissolves readily in an excess of the precipitant. From this solution alcohol precipitates potassic cobaltous cyanide, $K_4Co(C_6N_6)$, which crystallises in deep red, deliquescent needles. Exposed to air it eagerly absorbs oxygen, and is converted into potassic cobalticyanide, which is also formed with evolution of hydrogen on boiling the solution:

$$2K_4Co(C_6N_6) + 2H_2O = K_6Co_2(C_{12}N_{12}) + 2KOH + H_2,$$

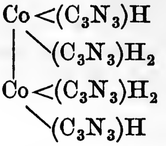
as also by heating freshly precipitated cobaltous hydrate with potassic cyanide solution:

$$12KCN + 2Co(OH)_2 + 2H_2O = K_6Co_2(C_{12}N_{12}) + 6KOH + H_2.$$

Potassic cobalticyanide crystallises in clear yellow crystals, isomorphous with those of potassic ferricyanide (see later), which dissolve easily in water, and on ignition decompose into potassic cyanide, cyanogen, nitrogen, and cobalt carbide. The cobalt in this compound cannot be recognised by any of its usual reagents. On adding a slight excess of sulphuric acid to a concentrated solution of this salt, and then much alcohol, potassic sulphate separates, and the alcoholic liquid yields, on evaporation, colourless needles of *hydrocobalticyanic acid*, $H_6Co_2Cy_{12},H_2O$, which loses its water of crystallisation at 100°, deliquesces in the air, reacts strongly acid, and not only decomposes carbonates, but dissolves zinc and iron with evolution of hydrogen. The difference in behaviour of nickel and cobalt salts with potassic cyanide, is made use of in the quantitative separation of these metals.

By saturation of hydrocobalticyanic acid with carbonates or hydrates of metals, or by double decomposition of salts of heavy metals, and solutions of potassic cobalticyanide, metallic cobalticyanides are obtained.

The probable constitutional formulæ of the cobalticyanides would represent them as containing tri-cyanogen groups; for instance, hydrocobalticyanic acid may be written:



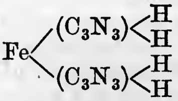
$$\begin{array}{l} Co<(C_3N_3)H \\ |\ \diagdown(C_3N_3)H_2 \\ Co<(C_3N_3)H_2 \\ \quad\diagdown(C_3N_3)H \end{array}$$

85. *Cyanides of Iron.*—Simple cyanides of this metal, corresponding to the chlorides, are almost unknown. By precipitation of a ferrous salt with potassic cyanide, a rust-coloured body is obtained, soluble in hydrochloric acid, which appears to be ferrous cyanide. On mixing a ferric salt with potassic cyanide solution, the liquid at first remains clear, and may in this state contain ferric cyanide; but it soon deposits ferric hydrate, with evolution of hydrocyanic acid, and contains, when an excess of potassic cyanide was employed, together with that salt, potassic ferrocyanide, $K_4FeC_6N_6$. This latter compound results also when ferrous salts are mixed with a large excess of potassic cyanide, and is obtained in crystals on evaporating the liquid.

86. *Hydro-ferrocyanic Acid,* $H_4Fe(C_6N_6)$.—If a concentrated solution of potassic ferrocyanide be acidulated with strong hydrochloric acid, colourless leafy crystals of hydro-ferrocyanic acid separate, whose quantity is greatly increased on addition of ether to the liquid.

It is soluble in water and alcohol, insoluble in ether, and on addition of excess of ether, to an alcoholic solution, is obtained in large crystals, colourless if air be completely excluded. In the air it quickly decomposes by oxidation, with blue colouration; it reacts and tastes strongly acid, decomposes carbonates, and forms the respective ferrocyanides with iron and zinc, hydrogen being evolved. In both acid and salts the iron is completely masked, i.e. not recognisable by its usual reagents.

In hydro-ferrocyanic acid also the cyanogen is probably in the form of bicyanogen, and the rational formula of the compound will therefore be:



$$Fe\begin{array}{l} \diagup(C_3N_3)<^{H}_{H} \\ \diagdown(C_3N_3)<^{H}_{H} \end{array}$$

In the ferrocyanides the hydrogen is replaced by metals, &c.

87. *Potassic Ferrocyanide,* $K_4Fe(C_6N_6),3H_2O$.—This important salt, known in commerce as *yellow prussiate,* was first obtained by washing carbonised blood. It crystallises in yellow quadratic pyramids, with basal faces most developed, with marked cleavage, parallel to the latter, into somewhat pliable laminæ. It is unalterable in air; 100 parts of water dissolve in the cold 25 parts of the salt, at the boiling temperature about double as much. On gentle heating the crystals lose their water and become white and opaque. The decomposition on strong ignition has already been referred to (§ 79).

The salt is formed on the large scale by introducing animal charcoal (from blood, horn, leather parings, &c.) and iron into fused pearlash (potassic carbonate). On strong ignition potassic cyanide is formed with evolution of gas:

$$K_2CO_3 + 4C + 2N = 3CO + 2KCN,$$

and from the sulphates in the pearlash and the iron, ferrous sulphide is formed. The cooled 'melt' is heated with hot water, whereby, according to the equation

$$6KCN + FeS = K_2S + K_4FeC_6N_6,$$

potassic ferrocyanide results, which is obtained on evaporation of the liquid in well-formed crystals, and is purified by re-crystallisation.

88. With salts of the heavy metals, potassic ferrocyanide generally yields amorphous, insoluble precipitates of the ferrocyanides; if the metallic solution be in excess all the potassium is replaced:

$$2CuSO_4 + K_4Fe(C_3N_3)_2 = 2K_2SO_4 + Cu_2Fe(C_3N_3)_2,$$

whilst, on the contrary, by careful addition of the metallic salt to potassic ferrocyanide precipitates are obtained, in which the potassium is only partly replaced:

$$CuSO_4 + K_4Fe(C_3N_3)_2 = K_2SO_4 + K_2CuFe(C_3N_3)_2.$$

By boiling with potassic hydrate solution, the insoluble metallic ferrocyanides are converted into potassic ferrocyanide, and the insoluble hydrate or oxide of the metal:

$$Cu_2Fe(C_3N_3)_2 + 4KOH = K_4Fe(C_3N_3)_2 + 2CuO + 2OH_2.$$

If other alkalies or alkaline earths be employed, the ferrocyanides of these metals result:

$$Cu_2Fe(C_3N_3)_2 + 2Ba(HO)_2 = Ba_2Fe(C_3N_3)_2 + 2CuO + 2OH_2.$$

89. *Sodic ferrocyanide*, $Na_4Fe(C_3N_3)_2,12OH_2$, crystallises in yellow, monoclinic, readily soluble crystals, which effloresce on exposure to air.

Ammonic ferrocyanide, $(NH_4)_4Fe(C_3N_3)_2,3H_2O$, is isomorphous with the potassium salt.

Baric ferrocyanide, $Ba_2Fe(C_3N_3)_2,6H_2O$, is difficultly soluble in cold water; somewhat more readily soluble are $Sr_2Fe(C_3N_3)_2,15OH_2$, $Ca_2Fe(C_3N_3)_2,12H_2O$, and $Mg_2Fe(C_3N_3)_2,10H_2O$.

Of the insoluble ferrocyanides of the heavy metals, the following may be shortly noticed:

Zincic-ferrocyanide, $Zn_2Fe(C_3N_3)_2,3H_2O$, is a white amorphous precipitate, as is also the cadmic salt.

Nickelous ferrocyanide, greenish white, *cobaltic ferrocyanide*, yellowish green, *manganous ferrocyanide,* whitish, *cupric ferrocyanide,* $Cu_2Fe(C_3N_3)_2,7H_2O$, and *potassic cupric ferrocyanide,* $K_2CuFe(C_3N_3)_2$, are intensely red-brown amorphous precipitates; *plumbic ferrocyanide,* $Pb_2Fe(C_3N_3)_2,3H_2O$, and *argentic ferrocyanide,* $Ag_4Fe(C_3N_3)_2$, are white.

90. The *ferrocyanides of iron* require more detailed notice.

On mixing a soluble ferrocyanide with a ferrous salt, with total exclusion of oxygen, white precipitates of *ferrous ferrocyanide,* $Fe_2Fe(C_3N_3)_2$, and *potassic ferrous ferrocyanide,* $FeK_2Fe(C_3N_3)_2$, are obtained. The latter compound is always formed in the preparation of hydrocyanic acid by heating potassic ferrocyanide with dilute sulphuric acid (§ 74). Both bodies on treatment with potassic hydrate give potassic ferrocyanide with separation of ferrous hydrate:

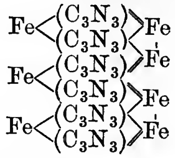
$$K_2Fe.Fe(C_3N_3)_2 + 2KOH = K_4Fe(C_3N_3)_2 + Fe(OH)_2,$$

and oxidise with great readiness on exposure to air, yielding blue ferric ferrocyanide.

When poured into solutions of ferric salts, potassic ferrocyanide gives a beautiful blue precipitate of ferric ferrocyanide, or Prussian blue:

$$3K_4Fe(C_3N_3)_2 + 2Fe_2Cl_6 = 12KCl + Fe_7C_{28}N_{18}$$

$$\text{or } \overset{\text{III}}{Fe}_4\,(FeC_6N_6)_3 =$$



Prussian blue is a deep blue powder, which, when air-dried, still contains more than 20% of water; when strongly compressed, and especially by rubbing with hard polished substances, it shows on the surface a copper-red metallic lustre. It is insoluble in water, alcohol, dilute acids, &c., but is dissolved by oxalic acid, and by ammonic acetate to blue solutions (blue ink). By boiling with alkalies it is re-converted into alkaline ferrocyanides, ferric hydrate separating:

$$(Fe_2)_2.3[Fe(C_3N_3)_2] + 12KHO = 3K_4Fe(C_3N_3)_2 + 2Fe_2(OH)_6.$$

When excess of potassic ferrocyanide is gradually mixed with a ferric solution, the so-called *soluble Prussian blue* is formed; a ferric potassic ferrocyanide, of unknown composition, which is insoluble in hydrochloric acid, but soluble in pure water to a deep blue liquid.

91. *Potassic Ferricyanide,* or *Red Prussiate,* $K_6Fe_2C_{12}N_{12} = K_6Fe_2(C_3N_3)_4$.—When chlorine is passed into a solution of potassic ferrocyanide until a portion of the liquid no longer gives a blue precipitate with ferric chloride, and the solution evaporated to crystallisation, potassic ferricyanide crystallises out in large, shining red, rhombic prisms, the salt being formed according to the equation:

$$2K_4Fe(C_3N_3)_2 + Cl_2 = 2KCl + K_6Fe_2(C_3N_3)_4.$$

Longer treatment with chlorine decomposes the ferricyanide.

The yellowish-greenish-brown solution of this very poisonous salt decomposes on exposure to light, with formation of potassic ferrocyanide and a blue precipitate; in the presence of free alkalies it acts as a powerful oxidising agent, being itself reduced to ferrocyanide; for instance:

$$K_6Fe_2(C_3N_3)_4 + Pb(OH_2) + 2KOH = 2K_4Fe(C_3N_3)_2 + PbO_2 + 2OH_2.$$

Potassic ferricyanide dissolves in 3·8 parts of cold, more readily in hot water; it precipitates the solutions of most salts of the heavy metals, the latter replacing the potassium. A large number of the resulting insoluble ferricyanides are characteristic, but others are the same colours as the ferrocyanides. The zinc and cadmium compounds are more or less deep yellow precipitates, soluble in dilute hydrochloric acid; of similar colour, but insoluble in HCl, are nickelous and cupric ferricyanides; cobaltous and manganous ferricyanides are dark brown, argentic ferricyanide is a rust-brown precipitate.

On addition of ferrous salts to potassic ferricyanide solution, a precipitate of ferrous ferricyanide (Turnbull's blue), similar to Prussian blue in appearance, is obtained:

$$K_6Fe_2(C_3N_3)_4 + 3FeSO_4 = 3K_2SO_4 + Fe_3Fe_2(C_3N_3)_4.$$

When insoluble metallic ferricyanides are heated with alkalies, the oxides are separated, and alkaline and iron cyanogen compounds formed; the latter are ferricyanides if the resulting oxide be not further oxidisable:

$$Zn_3Fe_2(C_3N_3)_4 + 6KOH = K_6Fe_2(C_3N_3)_4 + 3Zn(OH)_2,$$

whilst, on the other hand, if the metal admits of further oxidation, this ensues with reduction of the ferricyanide to ferrocyanide:

$$\overset{\text{III}}{Fe_3}\overset{\text{III}}{Fe_2}(C_3N_3)_4 + 8KOH = K_6\overset{\text{III}}{Fe_2}(C_3N_3)_4 + 3Fe(OH)_2 + 2KOH$$
$$= 2K_4Fe(C_3N_3)_2 + Fe_2(OH)_6 + Fe(OH)_2.$$

The soluble ferricyanides are not precipitated by ferric or chromic salts, as the respective ferricyanides are soluble in water:

$$K_6\overset{\text{III}}{Fe_2}(C_3N_3)_4 + Fe_2Cl_6 = 6KCl + Fe_2.Fe_2(C_3N_3)_4.$$

On mixing concentrated solutions of potassic ferricyanide and plumbic nitrate, heavy, soluble, dark crystals of *plumbic ferricyanide* slowly separate. When these crystals are decomposed by a not quite equivalent quantity of sulphuric acid, the liquid decanted from the precipitate of plumbic sulphate contains *hydroferricyanic acid*, $H_6Fe_2(C_3N_3)_4$, which, by careful evaporation in the cold, yields brown-coloured needles, easily soluble, strongly acid, and poisonous. Their solution gives with ferrous salts a blue precipitate, and decomposes on boiling with evolution of hydrocyanic acid and precipitation of a beautiful green-coloured insoluble ferrous ferric cyanide.

92. *Nitro-prusside Compounds.*—When powdered potassic ferrocyanide is heated with double its weight of fuming nitric acid, and an equal volume of water, carbonic anhydride, nitrogen, and hydrocyanic acid are evolved, and the solution no longer gives a blue precipitate with ferric salts; on cooling, potassic nitrate crystallises out. The dark-coloured liquid, diluted with water, and neutralised with sodic carbonate, is then evaporated nearly to crystallisation, then mixed with three times its volume of alcohol, filtered after long standing, and the solution evaporated. There then separate well-formed, red, rhombic prisms of sodic nitro-prusside, which are easily soluble in water. The same salt is obtained directly by adding to a solution of sodic ferrocyanide, potassic nitrite, ferric chloride, and very dilute sulphuric acid, and after many days' standing, neutralising with sodic hydrate.

The formula of sodic nitro-prusside is not yet settled with certainty. The simplest passably correct expression for the composition of the salt is $Na_2Fe(NO)C_5N_5,2H_2O$, but this does not correspond sufficiently well with the known decompositions of the salt. When heated with sodic hydrate, one-sixth of the contained iron separates as ferric hydrate, and the nitrosyl group separates as nitrite, whilst sodic ferrocyanide remains in solution. It can therefore be viewed as ten molecules of sodic ferrocyanide, in which six atoms of sodium are replaced by the ferric group $\overset{|||}{Fe_2}$, and ten more by (NO.) Thereby it would have the very complicated formula:

$$Na_{24}Fe_2(NO)_{10}[Fe(C_3N_3)_2]_{10},20H_2O.$$

The solution of sodic nitro-prusside decomposes spontaneously on long standing, with separation of Prussian blue. With many metallic salts it gives insoluble precipitates—e.g. with cupric salt a yellowish-green *cupric nitro-prusside*, with silver salt a flesh-coloured *argentic nitro-prusside*, $Ag_2(NO)Fe(C_5N_5)$ (?), from which, by careful decomposition with hydrochloric acid, there is obtained the unstable hydro-nitro-prussic acid $H_2(NO)Fe(C_5N_5)$ (?), of strongly acid reaction; by separation of this solution in vacuo, it crystallises in dark-red deliquescent prisms, which contain one molecule of water of crystallisation.

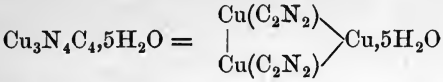
All soluble nitro-prussides give, with reducing agents, transient, beautiful violet or blue solutions. These colours are most easily produced by soluble metallic sulphides. Sodic nitro-prusside, therefore, is used as a very sensitive reagent for alkaline sulphides and hydric sulphide.

93. *Cyanides of Manganese and Chromium.*—Potassic manganocyanide, $K_4Mn(C_3N_3)_2,3H_2O$, isomorphous with the corresponding ferrous compound, results from the addition of potassic cyanide to manganous acetate, until the greenish precipitate of manganous cyanide first formed is re-dissolved, and subsequent precipitation with alcohol. It crystallises in transparent blue tables of the quadratic system, effloresces in dry air, and dissolves easily in water to a colourless liquid; the solution on standing yields a green insoluble double salt of the formula $K.Mn(C_3N_3)$ or $K_2Mn_2(C_3N_3)_2$.

On exposure to the air of a solution of potassic manganocyanide, oxygen is absorbed with formation of *potassic manganicyanide*, $K_6Mn_2(C_3N_3)_4$, which crystallises in deep red prisms, isomorphous with potassic ferricyanide.

By boiling a solution of six parts of potassic cyanide with five parts of chrome alum, addition of a tenth of the volume of liquid of alcohol, and evaporation of the filtrate, there is obtained *potassic chromicyanide*, $K_6Cr_2(C_3N_3)_4$, as easily soluble, clear, yellow, monoclinic crystals.

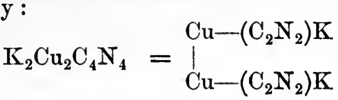
94. *Cyanides of Copper.*—A cyanide of copper of the formula $Cu(CN)_2$ is not obtainable in the pure state; an impure preparation is formed by addition of potassic cyanide to solution of cupric sulphate, or of cupric acetate to hydrocyanic acid, as a dirty yellowish-brown precipitate, but this very quickly decomposes, with evolution of cyanogen, into green crystals of *cuprous cupric cyanide*:



$$Cu_3N_4C_4,5H_2O = \begin{array}{l} Cu(C_2N_2) \\ | \\ Cu(C_2N_2) \end{array} > Cu,5H_2O$$

In boiling water this is readily further decomposed into cyanogen and *cuprous cyanide*, $Cu_2(CN)_2 = CN—Cu—Cu—CN$.

Cuprous cyanide is a white powder, insoluble in water, easily soluble in hydrochloric acid, ammonia, or aqueous potassic cyanide. With the latter it forms crystalline, colourless, double salts of different composition, namely:



$$K_2Cu_2C_4N_4 = \begin{array}{l} Cu—(C_2N_2)K \\ | \\ Cu—(C_2N_2)K \end{array}$$

which is difficultly soluble, and the more soluble $K_6Cu_2C_8N_8$, from which sulphuretted hydrogen does not precipitate the copper. These double salts are also obtained when solutions of cupric salts are mixed with excess of potassic cyanide.

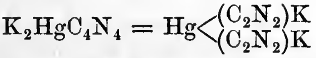
From plumbic cupro-cyanide (obtained by precipitation of potassic cupro-cyanide with plumbic acetate) the compound $H_2Cu_2C_4N_4$ is obtained by decomposition with sulphuretted hydrogen; it readily decomposes into cuprous cyanide and hydrocyanic acid.

95. Of the cyanogen compounds of mercury, that one corresponding to calomel is not known; when potassic cyanide is added to a mercurous salt, metallic mercury is precipitated, and mercuric cyanide left in solution:

$$Hg_2(NO_3)_2 + 2KCN = 2KNO_3 + Hg + Hg(CN)_2.$$

Mercuric cyanide is prepared by dissolving yellow mercuric oxide in aqueous hydrocyanic acid, the former being used in slight excess. It is also easily obtained by boiling Prussian blue with mercuric oxide, until all the iron is precipitated as oxide. At ordinary temperatures one part of $Hg(CN)_2$ is soluble in eight parts of water. It crystallises in large brilliant quadratic prisms, which are extremely poisonous; on heating it splits up into metal, and cyanogen gas, a portion of which remains polymerised as paracyanogen, a blackish-brown powder.

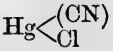
Mercuric cyanide yields with the alkaline cyanides beautiful crystalline double salts, e.g.



$$K_2HgC_4N_4 = Hg<\begin{array}{l} (C_2N_2)K \\ (C_2N_2)K \end{array}$$

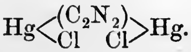
which crystallises in colourless octahedra.

By mixing its solution with the molecular quantity of mercuric chloride and evaporating, quadratic prisms separate, of *mercuric cyanochloride*



$$Hg<\begin{array}{l} (CN) \\ Cl \end{array}$$

or more probably

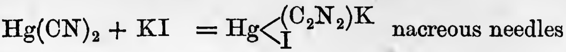


$$Hg<\begin{array}{cc} \multicolumn{2}{c}{(C_2N_2)} \\ Cl & Cl \end{array}>Hg.$$

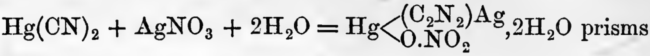
On boiling mercuric cyanide solution with mercuric oxide, much of the latter is dissolved, and on cooling, needles of *mercuric oxycyanide*, $(CN)-Hg-O-Hg-(CN)$, separate.

Mercuric cyanide also combines with many metallic chlorides, bromides, and iodides, forming double salts, most of which crystallise beautifully; for instance:

$$Hg(CN)_2 + NaCl = Hg{<}^{(C_2N_2)Na}_{Cl} \quad \text{silky flattened needles}$$



$$Hg(CN)_2 + KI = Hg{<}^{(C_2N_2)K}_{I} \quad \text{nacreous needles}$$



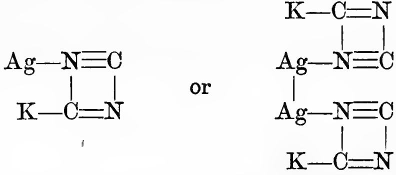
$$Hg(CN)_2 + AgNO_3 + 2H_2O = Hg{<}^{(C_2N_2)Ag}_{O.NO_2},2H_2O \quad \text{prisms}$$

96. *Argentic cyanide*, $Ag(CN)$ or $Ag_2(C_2N_2)$, separates as a white curdy precipitate, resembling argentic chloride, when hydrocyanic acid or a soluble cyanide is added to a silver solution. It is insoluble in water, and nitric acid, but easily soluble in ammonia, and potassic cyanide, and is unaltered by alkaline hydrates and chlorides. It does not blacken in sunlight, melts on heating, and leaves, on long ignition in absence of air, a white metallic mass consisting of silver and argentic paracyanide, $Ag(C_3N_3)$.

As will be shown later, when treating of the nitrogen compounds of the alcohol radicals, the silver in argentic cyanide is most probably combined to the nitrogen, the cyanogen being present in the *iso* form, and the formula therefore:

$$C\equiv N-Ag.$$

The product of the solution of argentic in potassic cyanide is *potassic-argentic cyanide*, $KAg(CN)_2$, or $K_2Ag_2(C_2N_2)_2$, which crystallises in six-sided, colourless tables, readily soluble in water. In this compound there is probably a dicyanogen radical, consisting of one true and one isocyanogen group:



or

This salt is chiefly employed in electroplating, as it gives a very coherent deposit on the negative pole, when electrolised.

The behaviour of argentic cyanide towards potassic cyanide yields a method of sufficient accuracy for the estimation of hydrocyanic acid or potassic cyanide. For this purpose a measured quantity of the liquid under examination is taken and converted, if needful, into potassic cyanide, by addition of potassic hydrate. Dilute standard solution of argentic nitrate is then added slowly; at first there is no precipitate, potassic argentic cyanide being formed until one-half of the cyanogen is converted into argentic cyanide:

$$2KCN + AgNO_3 = KNO_3 + K.Ag.C_2N_2;$$

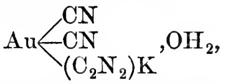
as soon, however, as by addition of silver solution this point is overstepped, every drop added produces a permanent precipitate of argentic cyanide:

$$KAg(C_2N_2) + AgNO_3 = 2Ag(CN) + KNO_3$$

The quantity of silver solution used up to this point corresponds therefore in equivalents to half the quantity of hydrocyanic acid present. As a rule, a decinormal solution of argentic nitrate is employed; this is prepared by dissolving 17·0 grams of argentic nitrate (an equivalent in $\frac{1}{10}$ grams) to one litre of solution ($= 0·017$ grams $AgNO_3$ per c.c.), and this is delivered drop by drop until the precipitate formed does not disappear on shaking. The number of c.c. used multiplied by ·0054 gives the amount in grams of prussic acid present (equivalent of $HCN = 27$ and $27 \times 2 = 54$), by ·013 the amount of potassic cyanide.

97. *Cyanides of Gold.—Aurous cyanide*, $Au(CN)$, a yellow powder consisting of microscopical hexagonal tables, insoluble in water, is best obtained by decomposition with hydrochloric acid, of its double salt with potassic cyanide. *Potassic aurocyanide* is easily prepared by solution of the oxide or sulphide in potassic cyanide, as also by long standing of finely divided gold in potassic cyanide solution, air being excluded. It forms long colourless prisms easily soluble in water.

Potassic auricyanide, $KAu(CN)_4$, H_2O or



$$Au\left\langle\begin{matrix}CN\\CN\\(C_2N_2)K\end{matrix}\right.,OH_2,$$

is obtained by mixing a neutral solution of auric chloride with a boiling concentrated solution of potassic cyanide; on cooling large colourless crystals are formed. The dilute aqueous solution generally obtained by mixing auric chloride and dilute potassic cyanide solution, is employed in electro-gilding.

When a solution of potassic auricyanide is added to argentic nitrate, a curdy precipitate of argentic auricyanide is obtained, which, suspended in water, and decomposed by a slightly insufficient quantity of hydrochloric acid, yields a solution of hydroauricyanic acid; by evaporation of the filtered solution *in vacuo*, large tabular crystals of auric cyanide, $Au(CN)_3,3H_2O$, are obtained.

98. *Cyanides of Platinum.*—Platinous chloride dissolves readily in aqueous potassic cyanide; on evaporation, potassic platinocyanide crystallises out:

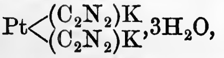
$$PtCl_2 + 4K(CN) = 2KCl + K_2Pt(C_4N_4).$$

It is also formed when a mixture of platinic chloride and potassic cyanide are boiled together for a long time:

$$PtCl_4 + 6KCN = K_2Pt(C_4N_4) + C_2N_2 + 4KCl,$$

or when spongy platinum is fused with potassic cyanide or ferrocyanide, the product extracted with water, and the solution crystallised.

Potassic platinocyanide,



$$Pt\left\langle\begin{matrix}(C_2N_2)K\\(C_2N_2)K\end{matrix}\right.,3H_2O,$$

forms long prisms, pale yellow by transmitted, beautiful blue-coloured by reflected light. By double decomposition other metallic platinocyanides are obtained from this, which when crystallised show splendid fluorescent phenomena; for instance:

Baric platinocyanide, $BaPt(C_4N_4),4H_2O$, citron yellow prisms with violet and greenish reflection.

Magnesic platinocyanide, $MgPt(C_4N_4),7H_2O$, red quadratic prisms, with metallic green reflection from the side faces, and deep blue from the end faces.

In aqueous solution these salts give insoluble precipitates with many of the salts of the heavy metals. By decomposing argentic or mercuric platinocyanide with hydric sulphide, the readily soluble hydroplatinocyanic acid, $H_2Pt(C_4N_4)$, is obtained, which crystallises when anhydrous in needles of golden lustre, when with $5H_2O$, in vermillion-coloured crystals with bluish-black reflection; the solution is colourless. Heated to higher temperatures, hydro-platinocyanic acid yields prussic acid, and leaves a residue of greenish-yellow insoluble platinous cyanide, which on stronger ignition is completely decomposed.

When chlorine is passed into a concentrated solution of potassic platinocyanide, there separates from the colourless liquid copper-coloured crystals of metallic lustre, consisting of potassic platinicyanide, $K_4Pt_2(C_{10}N_{10}),6H_2O$.

The cyanide corresponding to platinic chloride does not appear to exist.

HALOGEN COMPOUNDS OF CYANOGEN.

99. The cyanogen radical combines with chlorine, bromine, and iodine to haloid compounds, in which the halogen atom is united to the carbon. The chloride and bromide polymerise—the latter indeed only on heating—with tripling of the molecule.

Cyanogen chloride, $\mathrm{Cl{-}C{\equiv}N}$, or liquid cyanogen chloride, results from the decomposition of metallic cyanides and dilute prussic acid by chlorine. It is generally obtained by passing chlorine, in the dark, over damp mercuric cyanide:

$$Hg(CN)_2 + 2Cl_2 = HgCl_2 + 2ClCN,$$

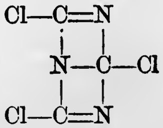
and condensation of the dried vapour in strongly cooled vessels; or by passing a quick stream of chlorine into aqueous prussic acid of 20% strength, the reaction taking place in a retort cooled by a freezing mixture, and connected with a condenser. The oily cyanogen chloride, which separates to the bottom, is parted from the aqueous liquid, mixed with mercuric oxide to remove any undecomposed HCN, and rectified into well-cooled receivers.

It is a colourless mobile liquid, becoming a crystalline mass at −6°, and boiling at 15·5°. Its vapour attacks the mucous membrane violently, and is in the highest degree poisonous; it is more difficultly soluble in water than in alcohol or ether.

By long keeping in sealed tubes, cyanogen chloride changes spontaneously into

Tricyanogen trichloride or *solid cyanogen chloride*:

$C_3N_3Cl_3 =$



The same compound is obtained directly by pouring anhydrous prussic acid into a flask filled with chlorine, and then exposing to sunlight; or when a slow stream of chlorine is passed into a solution of anhydrous prussic acid in four times its volume of ether, which is carefully cooled.

Solid cyanogen chloride crystallises in large needles or leaves, which melt at 145°; the boiling point is about 190°, the vapour density = 6·33, being three times that of the single cyanogen chloride.

By decomposition of potassic or mercuric cyanides by bromine, cyanogen bromide, $Br{-}C{\equiv}N$, is obtained in the form of shining colourless needles or cubes, which easily volatilise. When these, either alone or dissolved in ether, are heated in sealed glass tubes to 130°–140° for several hours, they are converted into:

Tricyanogen tribromide, which melts at a little above 300°, and sublimes at a still higher temperature.

Cyanogen iodide, $I{-}C{\equiv}N$, crystallises in colourless needles, which sublimes easily, without previous fusion, with a strong odour, and, like the above-mentioned compounds, is very poisonous. It is obtained by sublimation of a mixture of mercuric cyanide and iodine. On adding iodine to a pretty concentrated solution of potassic cyanide, the liquid colours quickly and solidifies to a crystalline mass:

$$KCN + I_2 = KI + ICN,$$

from which the ICN is obtained by shaking with ether.

Cyanic Acids.

100. The true cyanic acid has the constitution of cyanogen hydrate:

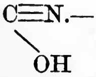
$$H{-}O{-}C{\equiv}N;$$

to this there would be a corresponding pseudo-cyanogen compound, carboxylimide:

$$O{=}C{=}N{-}H.$$

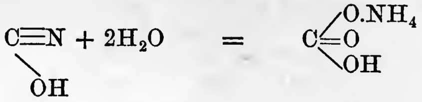
Which of these is the formula of the known cyanic acid is not yet quite certain, though there are good reasons for believing the first to be correct. On the other hand, two potassium derivatives, (CN)OK and (CO)NK, are known, which, though clearly different, easily change into one another.

The same is generally true of the polymeric acids, especially of tricyanic or cyanuric acid.

101. *Cyanic Acid,* HCNO, probably  $\underset{\diagdown OH}{C{\equiv}N}$.—Cyanic acid can only be obtained by strong heating of the polymeric cyanuric acid. This is done in a small retort, and the resulting vapour condensed in a receiver cooled with ice. It is a colourless, easily volatile liquid, of strongly acid reaction, smells like concentrated acetic acid, and blisters the skin. Left to itself, it clouds with slowly increasing temperature, and finally solidifies, with stronger evolution of heat, to a white porcelain-like mass, called *cyamelide.* This is a polymer of cyanic acid, but of unknown molecular weight; it has no longer the properties of an acid; by strong heating it is re-converted into cyanic acid.

When cyanic acid is mixed with water at the ordinary temperature they soon react, with evolution of heat, forming hydric-ammonic carbonate, so that the first acid reaction is quickly changed to alkaline:

$$CNHO + 2H_2O = NH_4.HCO_3$$



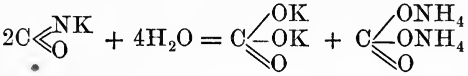
At 0° this reaction only takes place very slowly.

With the basic hydrates cyanic acid yields salts of neutral reaction, which require re-investigation for the proper determination of their structure.

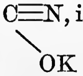
102. *Potassic Cyanate.*—(*a*) Ordinary potassic cyanate, or probably pseudo-cyanate, O═C═N—K, is formed by the oxidation of fused potassic cyanide by the air, or by metallic oxides. Usually potassic cyanide is melted and dry plumbic oxide, or minium, added, stirring until gas bubbles begin to appear:

$$KCN + PbO = KCNO + Pb.$$

Another method is to mix dried potassic ferrocyanide with half its weight of pyrolusite, and heat on an iron plate until the mass softens. The 'melt' is then treated with boiling hydrated alcohol (80%); from this solution the salt crystallises on cooling in colourless indistinct needles or leaves. It dissolves easily in water, difficultly in strong alcohol. Boiled with water it yields potassic and ammonic carbonates:



This cyanate, prepared by fusion, doubtless consists, at least in great part, of isocyanate, as by replacement of the potassium by hydrocarbon radicals, the isocyanic ethers result; for instance, $C\ll^{N.C_2H_5}_{O}$, in which the organic radical is united to the nitrogen.

(*β*) An isomeric body, probably the true cyanate, , is formed, together with potassic chloride, by passing cyanogen chloride into potassic hydrate, the temperature being kept as low as possible:

$$Cl—C\equiv N + 2KOH = KOC\equiv N + KCl + H_2O\,;$$

it crystallises in long needles, and is converted by fusion into the foregoing, from which it is distinguished by its convertibility into dicyandiamide (§ 115).

On endeavouring to liberate the acid from either of these salts, or from other metallic cyanates, by addition of strong mineral acids—for instance, sulphuric acid—carbonic anhydride is liberated with effervescence, whilst the acid sulphates of the respective metal, and of ammonium results:

$$K{-}N{=}C{=}O + 2H_2SO_4 + H_2O = CO_2 + KHSO_4 + (NH_4)HSO_4.$$
$$K{-}O{-}C{\equiv}N + 2H_2SO_4 + H_2O = CO_2 + KHSO_4 + (NH_4)HSO_4.$$

Ordinary potassic cyanide gives in aqueous solution white precipitates with the solutions of plumbic, argentic, and mercurous salts, and a green precipitate with cupric salts, of the respective isocyanates.

103. *Ammonic Cyanate.*—When cyanic acid vapour, and ammonia gas, both perfectly dry, are brought together in a dry balloon, they unite directly and form a snow-white woolly-crystalline powder, which, in fresh aqueous solution, with potassic hydrate, again gives ammonia and potassic cyanate, but on evaporation is converted into the isomeric urea (§ 130):

$$(NH_4).O{-}C{\equiv}N \quad = \quad O{=}C{<}^{NH_2}_{NH_2}$$

104. *Cyanuric Acid,* or *Tricyanic Acid,* $H_3C_3N_3O_3$, probably $(C_3N_3)(OH)_3$.—Under certain conditions cyanic acid polymerises into the triple molecule. When a solution of potassic cyanate is mixed with dilute acetic acid, hydric potassic cyanurate crystallises slowly out:

$$3KCNO + 2(HO.C_2H_3O) = KH_2C_3N_3O_3 + 2(KO.C_2H_3O),$$

from which cyanuric acid can be prepared. It is also most easily prepared from urea, which is heated until the mass at first melted solidifies. This is treated with cold water (Biuret, § 136), the residue dissolved in potassic hydrate, and the cyanuric acid liberated by means of hydrochloric acid. Urea, obtained as shown in the last paragraph, from a molecule of ammonia and a molecule of cyanic acid, splits up so that three molecules of it give up three molecules of ammonia, whilst the three cyanic acids polymerise to cyanuric acid:

$$3CON_2H_4 = 3NH_3 + C_3N_3H_3O_3.$$

Cyanuric acid crystallises in slightly acid, colourless crystals, with two molecules of water, which are given off at 100°; it is difficultly soluble in cold water, but can be crystallised from boiling water.

With metals it, like orthophosphoric acid, forms three series of salts:

Diacid salts	$MH_2C_3N_3O_3$
as in Monopotassic cyanurate	$KH_2C_3N_3O_3$
Monacid salts	$M_2HC_3N_3O_3$
as in Dipotassic cyanurate .	$K_2HC_3N_3O_3$
Normal salts	$M_3C_3N_3O_3$
as in Triargentic cyanurate .	$Ag_3C_3N_3O_3$

The salts of cyanuric acid are without exception crystallisable; those of the alkali metals are soluble in water, those of the heavy metals difficultly soluble or insoluble. The only normal salts known are those of lead and silver.

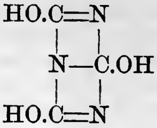
By heating as already mentioned, cyanuric acid is converted into cyanic acid:

$$H_3C_3N_3O_3 = 3HCNO.$$

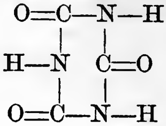
With phosphoric chloride it gives, on warming, solid cyanogen chloride:

$$C_3N_3O_3H_3 + 3PCl_5 = 3POCl_3 + 3HCl + C_3N_3Cl_3$$

This last reaction agrees better with the structural formula:



than with that for a tri-isocyanic acid:

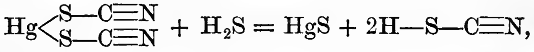


SULPHOCYANOGEN COMPOUNDS.

105. The alkaline salts of sulphocyanic acid are obtained from the alkaline cyanides by direct addition of sulphur, and the combination takes place not only by melting the ingredients, but even by boiling them together with water.

Sulphocyanic acid is obtained by addition of strong mineral acids to its salts; if an excess of the acid has been employed, it readily splits up into hydrocyanic acid and persulphodicyanic acid.

It is usually prepared by decomposition of its mercury salt by dry hydrochloric acid or hydric sulphide:



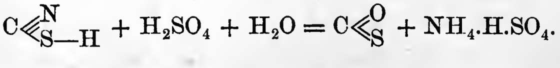
$$Hg\begin{matrix} \diagup S-C\equiv N \\ \diagdown S-C\equiv N \end{matrix} + H_2S = HgS + 2H-S-C\equiv N,$$

as a colourless liquid of pungent acetous odour, which solidifies at $-12{\cdot}5°$ to hexagonal plates. At higher temperatures (towards 100°) it boils, the greater part suffering the decomposition above mentioned. When damp, it decomposes into ammonic carbonate, carbonic disulphide, and hydric sulphide:

$$2(CN)SH + 3H_2O = (NH_4)_2CO_3 + CS_2$$

or $$(CN)SH + 3H_2O = (NH_4)HCO_3 + SH_2,$$

and yields carbonic oxysulphide by warming with very dilute sulphuric acid:



$$C\begin{matrix} \equiv N \\ -S-H \end{matrix} + H_2SO_4 + H_2O = C\begin{matrix} =O \\ =S \end{matrix} + NH_4.H.SO_4.$$

Its aqueous solution has a strongly acid reaction, and can only be kept, for any length of time, at low temperatures. It colours ferric salts blood-red, from formation of ferric sulpho-cyanate, and, on account of the intensity of this colour, is used, in the form of any of its soluble salts, to detect small traces of iron.

106. *Potassic sulphocyanate* is generally prepared by heating a mixture of forty-six parts of dry potassic ferrocyanide, seventeen parts potassic carbonate, and thirty-two parts of sulphur. The ignited mass is boiled with alcohol, and on cooling, the salt separates in long, clear, striated plates, which deliquesce in moist air, and melt on gently heating.

The ready formation of this salt is used as a means of detecting small quantities of sulphur. For this purpose, the substance to be tested for sulphur, or a sulphide, is heated with some dry potassic cyanide, the mass, when cold, extracted with water, the liquid rendered slightly acid and tested with ferric chloride; a blood-red colour shows the presence of sulphur.

Sodic sulphocyanate is prepared similarly to the potassium salt; it occurs in small quantity in saliva, and can be detected therein by ferric chloride.

107. *Ammonic sulphocyanate* is prepared on the large scale by boiling ammonic cyanide solution (wash-water from gas-works) with sulphur, also by heating carbonic disulphide with alcoholic ammonia:

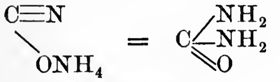
$$CS_2 + 4NH_3 = NH_4.SCN + (NH_4)_2S.$$

It is also easily formed by mixing prussic acid with yellow ammonic sulphide, and evaporating off the excess of the latter on the water bath:

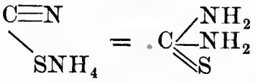
$$2HCN + (NH_4)_2S_3 = 2\,(NH_4)\,SCN + H_2S.$$

This last reaction affords an excellent means of testing for small quantities of prussic acid.

Ammonic sulphocyanate forms readily soluble crystals, quite similar to those of the potassic salt, which melt without change at 147°, and at 170° begin to suffer an analogous decomposition to that which occurs to ammonic cyanate at ordinary temperatures; namely, it forms sulphurea:



At ordinary temperatures in aqueous solution.



At 170°.

108. The sulphocyanates of the alkaline earths, and of the metals of the zinc and iron group, are soluble in water, partly also in alcohol. *Ferric sulphocyanate* is an uncrystallisable, nearly black, deliquescent mass, which dissolves in water and alcohol with deep blood-red colour. The sulphocyanates of copper, lead, silver, and mercury are obtained by double decomposition as insoluble precipitates. By mixing solutions of the mercury nitrates and potassic sulphocyanate, the respective mercury salts are obtained:

$Hg_2(SCN)_2$ mercurous sulphocyanate as amorphous
and $Hg(SCN)_2$ mercuric sulphocyanate as crystalline

black precipitates. Both burn on heating, with remarkable swelling and evolution of mercury vapour, and leave behind an extraordinary voluminous mass (Pharaoh's serpents) of crude mellone (§ 122).

109. The anhydride of sulphocyanic acid: *cyanogen sulphide,*

$(CN)_2S = S{<}\begin{smallmatrix}C\equiv N\\ C\equiv N\end{smallmatrix}$, is obtained in clear rhombic tables, by acting on argentic sulphocyanate with an ethereal solution of cyanogen iodide:

$$Ag{-}S{-}C{\equiv}N + I{-}C{\equiv}N = AgI + S\,(CN)_2,$$

and evaporating the liquid. It smells like the iodide, sublimes even at 30° in thin leaves, and fuses at 65°. It is soluble, unchanged in alcohol, ether, and carbonic disulphide. The aqueous solution decomposes readily with separation of a yellow powder. With potassic hydrate solution, cyanogen sulphide yields potassic cyanate and sulphocyanate:

$$(CN)_2S + 2KOH = KOCN + KSCN + H_2O.$$

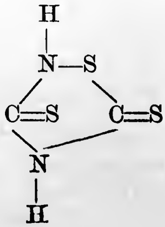
110. *Isosulphocyanic acid* is still unknown, but the potassic salt, $S{=}C{=}N{-}K$, is obtained by warming persulphocyanic acid (following paragraph) with alcoholic potassic hydrate, in the form of granular crystals, whose aqueous solution is not reddened by ferric salts, and yields coloured precipitates with cobalt, nickel, and cadmium salts. If the solution of the potassic salt is boiled for a long time, or if the dry salt be heated to melting, it is converted into the ordinary sulphocyanate The true sulphocyanates are more stable at high temperatures than the isosulphocyanates, whilst with the oxycyanates exactly the reverse is the case, probably in consequence of the greater affinity of oxygen for carbon.

111. *Persulphodicyanic acid* (persulphocyanic acid), $C_2N_2H_2S_3$, separates slowly in yellow needles, with evolution of hydrocyanic acid, when a saturated solution of potassic sulphocyanate is mixed with six times its bulk of concentrated hydrochloric acid:

$$3KSCN + 3HCl = 3KCl + HCN + H_2N_2C_2S_3.$$

The precipitate is purified by solution in dilute ammonia, and the ammonic salt so formed decomposed at the boiling temperature by hydrochloric acid. On cooling the compound crystallises in golden-yellow needles, difficultly soluble in boiling water. With the alkalies persulphocyanic acid forms, readily soluble, with many of the heavy metals, insoluble compounds; if, for instance, a hot solution of the acid be mixed with plumbic acetate, the lead salt is precipitated in the form of a deep yellow amorphous powder, of the formula $PbC_2N_2S_3$.

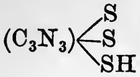
As the potassium salt of persulphocyanic acid, when warmed with alcoholic potassic hydrate, yields potassic isosulphocyanate (see § 110), it follows most probably that persulphocyanic acid must also be expressed as an iso compound $[(CS)NH]_2S$, whose structure would be



112. *Persulphocyanogen*, or *pseudosulphocyanogen*, $C_3HN_3S_3$. By action of strong nitric acid, chlorine, or bromine on a boiling solution of potassic sulphocyanate, persulphocyanogen separates as an orange-yellow, amorphous powder, insoluble in water, alcohol, or ether. When heated in a stream of chlorine, it yields, besides mellone and sulphur chloride, tricyanogen chloride; by heating with concentrated hydrochloric acid, it gives hydric sulphide, hydric persulphide, and cyanuric acid:

$$C_3H_3N_3S_3 + 3H_2O = H_2S + H_2S_2 + C_3N_3O_3H_3.$$

According to both reactions, it is a derivative of tricyanogen of the probable formula:

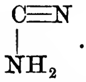


$$(C_3N_3)\begin{cases} S \\ S \\ SH \end{cases} = \textit{tricyanogen persulphide sulphhydrate.}$$

NITROGEN COMPOUNDS OF CYANOGEN.

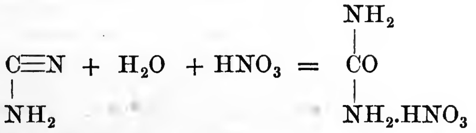
113. By combination of the carbon of true cyanogen, in both the single and polymerised modifications, with the nitrogen of ammonia residues, there results the amide compounds of cyanogen, of which the tricyanogen compounds are especially numerous.

Single Cyanamide Derivatives.



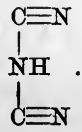
114. *Cyanamide*, $CN_2H_2 = \begin{matrix} C{\equiv}N \\ | \\ NH_2 \end{matrix}$. When the vapour of cyanogen chloride is passed into anhydrous ether saturated with ammonia, ammonic chloride immediately separates, and the ether contains cyanamide dissolved, which is obtained on evaporation in colourless, readily soluble crystals, melting at 40°. If the solution be decomposed by ammonia and argentic nitrate, a yellow precipitate of argentic cyanamide, $(CN)NAg_2$, is obtained.

From a solution acidulated with nitric acid, there separates, in a short time, leaf-like crystals of urea nitrate:

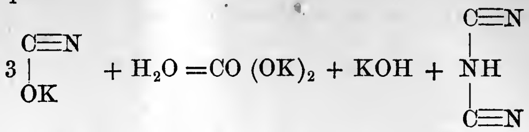


$$\begin{matrix} C{\equiv}N \\ | \\ NH_2 \end{matrix} + H_2O + HNO_3 = \begin{matrix} NH_2 \\ | \\ CO \\ | \\ NH_2.HNO_3 \end{matrix}$$

By the action of aqueous ammonia cyanamide polymerises to *dicyanodiamide*; by heating above its melting point, it is converted, with great evolution of heat, into *melamine*, and by warming with ammonic chloride, is changed into *guanadine hydrochlorate* (§ 127).



115. *Dicyanimide*, $C_2N_3H = \begin{matrix} C{\equiv}N \\ | \\ NH \\ | \\ C{\equiv}N \end{matrix}$. By long treatment of a solution of true potassic cyanate (§ 102) with potassic hydrate, dicyanimide is formed, together with the carbonate, probably according to the equation :

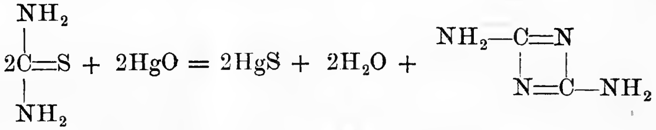


$$3\begin{matrix}C\equiv N\\ |\\ OK\end{matrix} + H_2O = CO\ (OK)_2 + KOH + \begin{matrix}C\equiv N\\ |\\ NH\\ |\\ C\equiv N\end{matrix}$$

It has not yet been obtained in a perfectly pure state, its existence being inferred from the result of adding argentic nitrate to the solution previously neutralised with nitric acid, when a white precipitate, not affected by light, is obtained, of the formula $(CN)_2NAg$.

Dicyanodiamide.

116. *Dicyanodiamide*, or *param*, $C_2N_4H_4 = (C_2N_2)\ (NH_2)_2$, results from the spontaneous polymerisation of cyanamide in aqueous ammoniacal solution. It is also formed by desulphurising sulphurea by mercuric or argentic oxides :



$$2\begin{matrix}NH_2\\ |\\ C=S\\ |\\ NH_2\end{matrix} + 2HgO = 2HgS + 2H_2O + \begin{matrix}NH_2-C=N\\ \quad\ |\quad\ |\\ N=C-NH_2\end{matrix}$$

It crystallises in colourless leaves, which melt unchanged at 205°, dissolve pretty easily in water and alcohol, but little in ether.

With argentic nitrate, dicyanodiamide yields a compound

$$C_2N_4H_4AgNO_3 = (C_2N_2)\!<\!\begin{matrix}NH_2\\ NH_2Ag.ONO_2,\end{matrix}$$

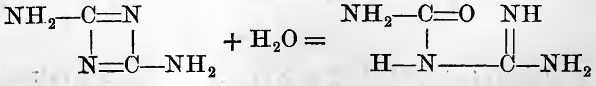
which on addition of ammonia is converted into argentic dicyanodiamide

$$(C_2N_2)\!<\!\begin{matrix}NH_2\\ NHAg.\end{matrix}$$

If a solution of dicyanodiamide be evaporated with hydrochloric acid, there remain large tables of dicyanodiamidine hydrochlorate :

$$(C_2N_2)\ (NH_2)_2 + H_2O + HCl = C_2H_6N_4O.HCl,$$

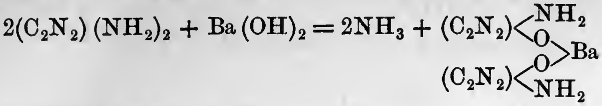
from which *dicyanodiamidine* can be separated. This latter is readily soluble in water, difficultly in alcohol, has strongly basic properties, and yields well-crystallised salts. It results from dicyanodiamide by the addition of the elements of water, probably according to the equation :



$$\begin{matrix}NH_2-C=N\\ \quad\ |\quad\ |\\ N=C-NH_2\end{matrix} + H_2O = \begin{matrix}NH_2-C=O\quad NH\\ \quad |\qquad\quad \|\\ H-N\text{——}C-NH_2\end{matrix}$$

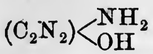
and is therefore a body intermediate between urea and guanidine (§ 127).

By boiling with baric hydrate dicyanodiamide is converted into the barium salt of dicyanamic acid:



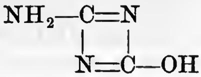
$$2(C_2N_2)(NH_2)_2 + Ba(OH)_2 = 2NH_3 + \begin{matrix}(C_2N_2)\begin{cases}NH_2\\O\end{cases}\\(C_2N_2)\begin{cases}O\\NH_2\end{cases}\end{matrix}\!\!>Ba$$

from which *dicyanamic acid*

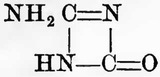


$$(C_2N_2)\begin{cases}NH_2\\OH\end{cases}$$

or



probably also a pseudocyanogen compound



is obtained by careful precipitation of the barium with sulphuric acid, and evaporation of the solution in long spear-like needles. Its potassic salt results directly by heating cyanamide with potassic cyanate to 60°:

$$(CN)NH_2 + CNKO = C_2N_3H_2KO.$$

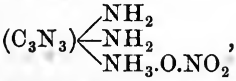
Amid Derivatives of Tricyanogen.

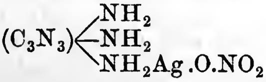
117. *Tricyanotriamide, melamine,* $(C_3N_3)(NH_2)_3$. Melamine is easily obtained by direct polymerisation of cyanamide on heating (§ 113). It is most simply obtained by strong heating of potassic sulphocyanate with ammonic chloride, or of ammonic sulphocyanate; on extracting the residue with water, melam $(C_6H_9N_{11})$ remains as an insoluble white powder, which, on boiling with potassic hydrate, splits up into melamine, and the potassic salt of ammeline:

$$C_6H_9N_{11} + KOH = C_3N_6H_6 + C_3H_4KN_5O.$$

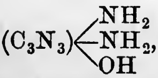
By cooling melamine separates out, whilst potassic ammelide remains dissolved.

Melamine crystallises in rhombic octahedra, which dissolve with difficulty in cold water, more easily in boiling water, and are insoluble in alcohol or ether. It unites with one equivalent of acid to difficultly soluble, well-crystallised salts of acid reaction, e.g.

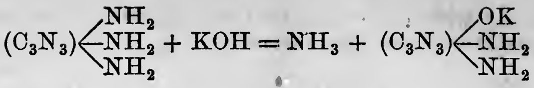




Melamine nitrate, $(C_3N_3)\begin{cases}NH_2\\NH_2\\NH_3.O.NO_2\end{cases}$, forms fine white silky needles; with argentic nitrate it gives a crystalline precipitate of argento-melamine nitrate, $(C_3N_3)\begin{cases}NH_2\\NH_2\\NH_2Ag.O.NO_2\end{cases}$

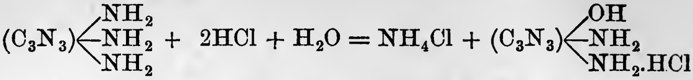


118. *Ammeline,* $(C_3N_3)\begin{cases}NH_2\\NH_2\\OH\end{cases}$, or *tricyanodiamide hydrate, cyanurdiamic acid,* results, together with ammonia, from the action of alkalies on melamine:



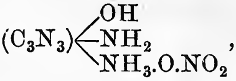
$$(C_3N_3)\left\langle\begin{array}{l}NH_2\\NH_2\\NH_2\end{array}\right. + KOH = NH_3 + (C_3N_3)\left\langle\begin{array}{l}OK\\NH_2\\NH_2\end{array}\right.$$

or, by boiling melamine with aqueous acids:

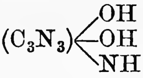


$$(C_3N_3)\left\langle\begin{array}{l}NH_2\\NH_2\\NH_2\end{array}\right. + 2HCl + H_2O = NH_4Cl + (C_3N_3)\left\langle\begin{array}{l}OH\\NH_2\\NH_2.HCl\end{array}\right.$$

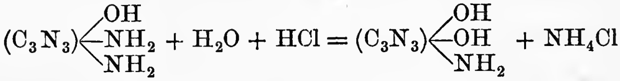
It is at the same time both an acid hydrate and a basic amide. As potassic salt it is obtained from melam together with melamine (§ 117). From the solutions of its alkaline salts, it is obtained by careful addition of acid, or, from its compounds with acids by neutralisation with alkali, or large addition of water, as a white crystalline powder, insoluble in water, alcohol, and ether. By evaporation of its solution in acids, crystalline salts are obtained, e.g.



Ammeline nitrate, $(C_3N_3)\left\langle\begin{array}{l}OH\\NH_2\\NH_3.O.NO_2\end{array}\right.$, in long four-sided prisms decomposed by water, with separation of ammeline.

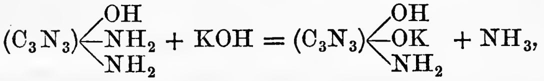


119. *Ammelide*, $(C_3N_3)\left\langle\begin{array}{l}OH\\OH\\NH_2\end{array}\right.$, *tricyano-amide dihydrate*, *cyanurmonaminic acid*, or *melanurenic acid*, is obtained by long-continued boiling of ammeline acid salts with free acids, or of ammeline with alkalies:



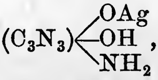
$$(C_3N_3)\left\langle\begin{array}{l}OH\\NH_2\\NH_2\end{array}\right. + H_2O + HCl = (C_3N_3)\left\langle\begin{array}{l}OH\\OH\\NH_2\end{array}\right. + NH_4Cl$$

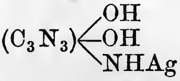
or



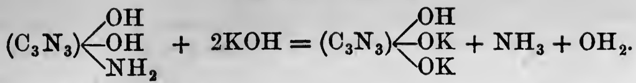
$$(C_3N_3)\left\langle\begin{array}{l}OH\\NH_2\\NH_2\end{array}\right. + KOH = (C_3N_3)\left\langle\begin{array}{l}OH\\OK\\NH_2\end{array}\right. + NH_3,$$

and is also obtained from urea by action of higher temperatures.



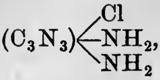


It is precipitated by acids from its alkaline salts, as a white powder insoluble in water, alcohol, and ether; it is somewhat soluble in ammoniacal liquids, and readily in potassic hydrate and concentrated acids. The acid and alkali salts of ammelide are decomposed by water, and are therefore not obtainable in the pure and crystallised state; nevertheless a silver derivative has been obtained by addition of argentic nitrate to an ammoniacal ammelide solution, as a white precipitate of the formula $C_3N_4H_3AgO_2$. Whether this should be formulated as a silver salt, $(C_3N_3)\left\langle\begin{array}{l}OAg\\OH\\NH_2\end{array}\right.$, or as an argento-amide, $(C_3N_3)\left\langle\begin{array}{l}OH\\OH\\NHAg\end{array}\right.$, has not yet been determined. By concentrated sulphuric acid, or by boiling with strong solution of potassic hydrate, ammelide is converted into a cyanurate:



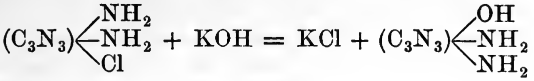
$$(C_3N_3)\left\langle\begin{array}{l}OH\\OH\\NH_2\end{array}\right. + 2KOH = (C_3N_3)\left\langle\begin{array}{l}OH\\OK\\OK\end{array}\right. + NH_3 + OH_2.$$

Cyanuric acid, therefore, is obtainable both from ammelide as above, and from melamine by fusion with potassic hydrate.

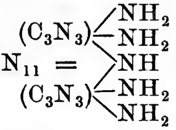
120. *Tricyanchlorodiamide*, or *chlorcyanuramide*, $C_3N_5H_4Cl$ or  $(C_3N_3)\left\langle\begin{array}{l}Cl\\NH_2\\NH_2\end{array}\right.$, results as a white, very difficultly soluble, crystalline powder, by action of ammonia on solid cyanogen chloride:

$$(C_3N_3)Cl_3 + 4NH_3 = 2NH_4Cl + (C_3N_3Cl(NH_2)_2.$$

Heated with dilute potassic hydrate it yields potassic chloride and ammeline:



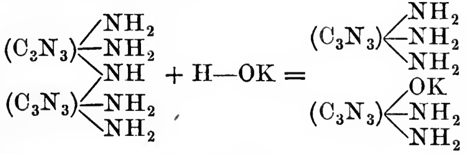
$$(C_3N_3)\left\langle\begin{array}{l}NH_2\\NH_2\\Cl\end{array}\right. + KOH = KCl + (C_3N_3)\left\langle\begin{array}{l}OH\\NH_2\\NH_2\end{array}\right.$$

121. *Melam*, $C_6H_9N_{11}$ =  $\begin{array}{l}(C_3N_3)\left\langle\begin{array}{l}NH_2\\NH_2\end{array}\right.\\ \quad\quad\quad\;\; >NH\\(C_3N_3)\left\langle\begin{array}{l}NH_2\\NH_2\end{array}\right.\end{array}$, the diamide-imide of tricyanogen, is formed, as already mentioned, by heating ammonic sulphocyanate together with hydric sulphide and ammonic sulphide:

$$6CNS.NH_4 = 5H_2S + NH_4.SH + C_6H_9N_{11},$$

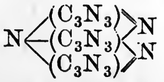
as a white powder insoluble in cold water, easily soluble in boiling water, from which it separates on cooling as a curdy precipitate.

By prolonged boiling with potassic hydrate it is decomposed into melamine and potassic ammelide:



$$\begin{array}{l}(C_2N_3)\left\langle\begin{array}{l}NH_2\\NH_2\end{array}\right.\\ \quad\quad\quad\;\; >NH\\(C_3N_3)\left\langle\begin{array}{l}NH_2\\NH_2\end{array}\right.\end{array} + H{-}OK = \begin{array}{l}(C_3N_3)\left\langle\begin{array}{l}NH_2\\NH_2\\NH_2\end{array}\right.\\(C_3N_3)\left\langle\begin{array}{l}OK\\NH_2\\NH_2\end{array}\right.\end{array}$$

122. *Mellone Compounds.*—On ignition of ammonic or mercuric sulphocyanates, persulphodicyanic acid, persulphocyanogen, melam, melamine, or ammeline, there is left a yellow powder—*mellone*, consisting essentially of a body of the composition C_9N_{12}; probably



$$N\left\langle\begin{array}{l}(C_3N_3)\\(C_3N_3)\\(C_3N_3)\end{array}\right\rangle\begin{array}{l}N\\N\end{array}$$

as it is slowly converted into cyanuric acid by boiling nitric acid.

If it be fused with potassic sulphocyanate, *tripotassic mellonide* results, which is derived from hydromellonic acid.

Potassic mellonide, $C_9N_{13}K_3$, is also formed by ignition of potassic sulphocyanate:

$$13KSCN = C_9N_{13}K_3 + 4CS_2 + 5K_2S,$$

but best if to the latter salt, when fused (seven parts), fused antimonious chloride (three parts) be slowly added in small portions, and at last the temperature raised sufficiently to fuse the resulting antimonious sulphide. When cold the mass is extracted with boiling water, any potassic sulphide removed by plumbic hydrate, and the liquid boiled and filtered; on cooling tripotassic mellonide crystallises in fine silky needles, which dissolve pretty easily in warm water, but not at all in alcohol or ether.

When the concentrated solution of this salt is mixed with acetic acid, dipotassic hydric mellonide crystallises out in glittering clinorhombic needles:

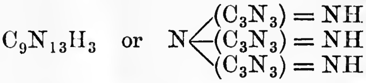
$$C_9N_{13}K_3 + HO.C_2H_3O = C_9N_{13}HK_2 + KO.C_2H_3O,$$

whilst hydrochloric acid gives, with the original solution, a white precipitate of dihydric potassic mellonide, $C_9N_{13}H_2K$.

The soluble potassic compound gives precipitates with the salts of heavy metals, e.g. argentic mellonide as a white precipitate, which, suspended in water and decomposed with hydric sulphide, yields argentic sulphide and hydromellone:

$$2C_9N_{13}Ag_3 + 3H_2S = 3Ag_2S + 2C_9N_{13}H_3.$$

Hydromellone, or *hydromellonic acid*:



$$C_9N_{13}H_3 \quad \text{or} \quad N\begin{cases}(C_3N_3) = NH\\(C_3N_3) = NH\\(C_3N_3) = NH\end{cases}$$

is readily soluble in water, reacts strongly acid, and decomposes on heating into ammonia and mellone:

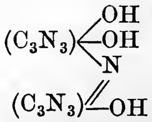
$$C_9N_{13}H_3 = NH_3 + C_9N_{12}.$$

123. *Cyameluric acid*, $C_6N_7O_3H_3$. By boiling tripotassic mellonide with concentrated solution of potassic hydrate, ammonia is evolved, and ammelide and potassic cyamelurate are formed:

$$C_9N_{13}K_3 + KOH + 4H_2O = \underset{\text{Potassic cyamelurate.}}{C_6N_7O_3K_3} + \underset{\text{Potassic ammelide.}}{C_3H_3KN_4O_2} + 2NH_2$$

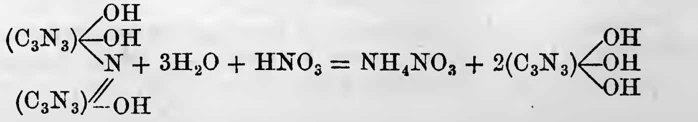
On cooling, potassic cyamelurate separates out in needle-shaped crystals from its solution; strong acids (mineral) precipitate *cyameluric acid* as a white crystalline precipitate, little soluble in cold, more readily in boiling water.

Cyameluric acid has, as a tricyanogen derivative, the structural formula:



$$\begin{array}{l}(C_3N_3)\begin{cases}OH\\OH\\N\end{cases}\\(C_3N_3)\begin{cases}/\!/\\OH\end{cases}\end{array}$$

It forms with metals tribasic salts, of which only those of the alkalies are soluble in water, and is converted into cyanuric acid by heating with strong mineral acids:



$$\begin{array}{l}(C_3N_3)\begin{cases}OH\\OH\\N\end{cases} + 3H_2O + HNO_3 = NH_4NO_3 + 2(C_3N_3)\begin{cases}OH\\OH\\OH\end{cases}\\(C_3N_3)\begin{cases}/\!/\\OH\end{cases}\end{array}$$

CYANOGEN AND PARACYANOGEN.

124. From its compounds with those metals whose oxides decompose on ignition with evolution of oxygen, cyanogen is split off on heating and is obtained as cyanogen gas and paracyanogen. Both bodies contain nitrogen and carbon only, and that in the same ratio; they consist not of single cyanogen groups, but of several such united with one another.

Cyanogen, or *dicyanogen*, C_2N_2 =  $\begin{array}{l} C\equiv N \\ | \\ C\equiv N \end{array}$, is most readily obtained by heating mercuric cyanide in a retort of difficultly fusible glass:

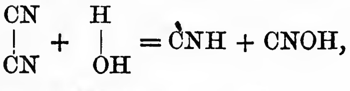
$$Hg{<}\begin{matrix}(CN)\\(CN)\end{matrix} = Hg + (CN)_2,$$

when it is evolved, together with easily condensible mercury vapour. A spongy black mass of paracyanogen is left in the decomposition apparatus.

Cyanogen is a colourless gas, has the density 1·864, and condenses at 0° under a pressure of $1\frac{1}{2}$ atmosphere to a clear liquid of specific gravity ·866, which boils at − 21°, and solidifies to a striated ice-like mass below − 34°. The odour of the gas is peculiar, and similar to that of prussic acid. Lighted in air, it burns with a blue, peach-edged flame to carbonic anhydride and nitrogen:

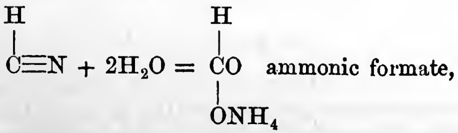
$$C_2N_2 + 2O_2 = 2CO_2 + N_2.$$

Water absorbs four to five times its volume, alcohol twenty-two times its volume of the gas. These solutions become dark-coloured on long standing, dark-brown flocks separating, which are soluble in alkalies and reprecipitated by acids. In the formation of this decomposition product, the elements of water take part, as oxygen and hydrogen are contained in it as well as carbon and nitrogen. The name *azulmic acid* has been given to it. There is formed at the same time in the solution ammonic oxalate, carbonate and formate, and urea. The formation of the ammonic formate is due to a decomposition into cyanic and prussic acids:



$$\begin{array}{c} CN \\ | \\ CN \end{array} + \begin{array}{c} H \\ | \\ OH \end{array} = CNH + CNOH,$$

which then partly further decompose:



$$\begin{array}{l} H \\ | \\ C\equiv N \end{array} + 2H_2O = \begin{array}{l} H \\ | \\ CO \\ | \\ ONH_4 \end{array} \text{ ammonic formate,}$$

$$CNOH + H_2O = CO_2 + NH_3.$$

The ammonia formed then combines with a part of the cyanic acid to form urea (§ 130), but otherwise also with water to convert still unaltered dicyanogen into azulmic acid.

Azulmic acid is formed in large quantities together with ammonic oxalate by action of cyanogen on aqueous ammonia.

On the other hand, by bringing together equal volumes of dry ammonia and cyanogen gases, they combine to form a black amorphous powder of the formula $C_4N_6H_6$, *hydrazulmine:*

$$2(C_2N_2) + 2NH_3 = C_4N_6H_6,$$

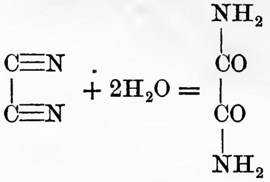
which is rapidly converted into azulmic acid by action of water

$$C_4N_6H_6 + H_2O = C_4N_5H_5O + NH_3,$$

the direct formation of the latter being represented by

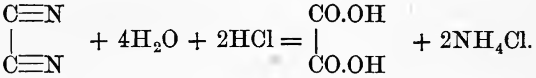
$$2C_2N_2 + H_2O + NH_3 = C_4N_5H_5O.$$

If an aqueous solution of cyanogen be mixed with some acetic aldehyde, it is completely converted into oxamide:



$$\begin{array}{l} C\equiv N \\ | \\ C\equiv N \end{array} + 2H_2O = \begin{array}{l} NH_2 \\ | \\ CO \\ | \\ CO \\ | \\ NH_2 \end{array}$$

whilst in presence of strong mineral acids it is converted into oxalic acid:



$$\begin{array}{l} C\equiv N \\ | \\ C\equiv N \end{array} + 4H_2O + 2HCl = \begin{array}{l} CO.OH \\ | \\ CO.OH \end{array} + 2NH_4Cl.$$

This transformation shows most strikingly that the carbon atoms in dicyanogen are joined together, and also that oxalic acid is a true dicarbonide.

There are indeed also other reactions known, by which the carbon atoms of dicyanogen are disunited, with formation of single cyanogen compounds; for instance, on passing dicyanogen through potassic hydrate, there is formed, besides potassic azulmate, considerable quantities of potassic cyanide and cyanate:

$$C_2N_2 + 2KOH = KCN + KCNO + OH_2;$$

on passing it over ignited potassic carbonate, potassic cyanate and isocyanate are formed:

$$\begin{array}{l} C\equiv N \\ | \\ C\equiv N \end{array} + \begin{array}{l} KO \\ KO \end{array}\!\!>C{=}O = \begin{array}{l} C\equiv N \\ | \\ K \end{array} + O{=}C{=}N{-}K + CO_2;$$

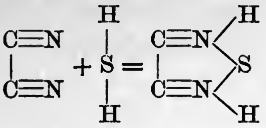
whilst potassium heated in cyanogen burns and forms potassic cyanide:

$$(CN)_2 + K_2 = 2KCN.$$

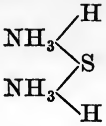
125. By the trivalent combination of the nitrogen to the carbon atoms, cyanogen appears as a double ammonia molecule, whose six hydrogen atoms are replaced by the hexavalent dicarbon group, C_2. In consequence of this method of saturation of the nitrogen atoms, the cyanogen molecule is able (like hydrocyanic acid) to form compounds, which are analogous in many ways to ammonia derivatives.

Especially noticeable amongst these are the compounds with hydric sulphide.

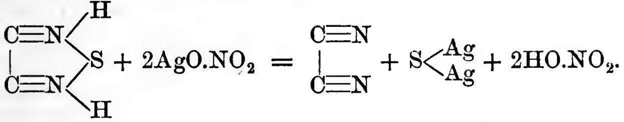
When equal volumes of cyanogen and hydric sulphide are mixed together in glass vessels, the sides of the latter are soon covered with yellow crystals of cyanogen monosulphhydrate, $C_2N_2H_2S$:



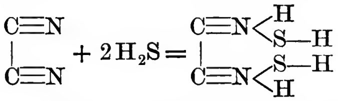
which correspond to ammonic sulphide



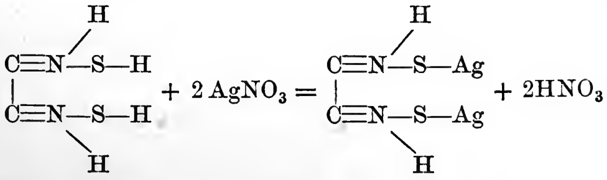
By heating their aqueous solution with silver salts, the compound is decomposed with evolution of cyanogen and precipitation of argentic sulphide :

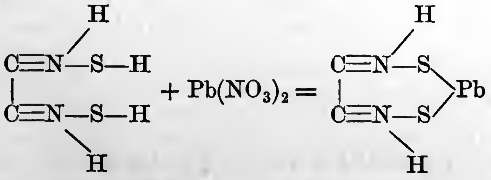


On passing cyanogen into a saturated solution of sulphuretted hydrogen until there is present one volume of the former to every two volumes of the latter, red needles of cyanogen disulphhydrate separate :



which corresponds to a doubled ammonic sulphhydrate. They are difficultly soluble in cold water, more easily in alcohol and ether. The aqueous solution gives coloured precipitates with lead and silver salts :





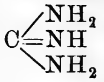
which yield the metallic sulphides on ignition.

126. *Paracyanogen*, $CxNx$, is, as already mentioned, a porous blackish substance left behind in the preparation of cyanogen gas from mercuric cyanide. It contains carbon and nitrogen only, and is polymeric to cyanogen. By strong ignition it is converted into cyanogen; by action of potassic hydrate it yields true potassic cyanate.

GUANIDINE, CN_3H_5.

127. *Guanidine* is a body genetically related to the cyanogen amides, as it contains a carbon atom whose four bonds are saturated by nitrogen, being united to three atoms of the latter.

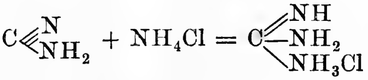
Guanidine is carbondiamide-imide:



$$C\left\langle\begin{matrix}NH_2\\ =NH\\ NH_2\end{matrix}\right.$$

It was originally prepared by the decomposition of guanine (see this) by chlorine, but later also obtained in many other ways. It is obtained from chloropicrin and orthocarbonic ether by action of ammonia, and by heating urea or biuret (§ 137) in an atmosphere of hydrochloric acid.

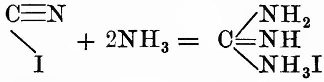
It is further obtained by action of an alcoholic cyanamide solution upon ammonic chloride at a temperature of 100°. According to the equation:



$$C\left\langle\begin{matrix}\equiv N\\ NH_2\end{matrix}\right. + NH_4Cl = C\left\langle\begin{matrix}=NH\\ NH_2\\ NH_3Cl\end{matrix}\right.$$

the hydrochloride is first formed, soluble in water and alcohol, from which guanidine is separated by argentic oxide.

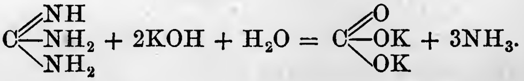
It is also easily obtained as the hydrodide by heating cyanogen iodide with alcoholic ammonia to 100°:



$$\begin{matrix}C\equiv N\\ \diagdown\\ I\end{matrix} + 2NH_3 = C\left\langle\begin{matrix}NH_2\\ =NH\\ NH_3I\end{matrix}\right.$$

It forms colourless crystals, readily soluble in water and alcohol, of strong alkaline taste. It absorbs carbonic anhydride from the air, and forms therewith a salt crystallising in beautiful quadratic prisms, $(CN_3H_5)_2H_2CO_3$. *Guanidine nitrate*, $CN_3H_5.HNO_3$, crystallises in colourless prisms, rather difficultly soluble in water. The hydrochloride yields with platinic chloride yellowish-red prisms, of the formula $2CN_3H_6Cl,PtCl_4$, easily soluble in water, and hydrated alcohol, difficultly soluble in anhydrous alcohol; with auric chloride beautiful long, deep-yellow needles, $CN_3H_6Cl, AuCl_3$, rather difficultly soluble in water.

By heating with concentrated alkaline solutions, it is resolved into ammonia and carbonic acid:



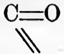
$$C\left\langle\begin{matrix}=NH\\ NH_2\\ NH_2\end{matrix}\right. + 2KOH + H_2O = C\left\langle\begin{matrix}=O\\ OK\\ OK\end{matrix}\right. + 3NH_3.$$

Similarly by action of strong acids under the influence of high temperatures:

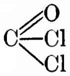
$$(CN_3H_5)_2H_2SO_4 + 2H_2SO_4 + 4H_2O = 3(NH_4)_2SO_4 + 2CO_2.$$

DERIVATIVES OF CARBONIC ACID AND CARBONIC DISULPHIDE.

128. Carbon monoxide is the common radical of the carbonic acid derivatives, and, as such, is termed *carboxyl*; it forms a true unsaturated compound :



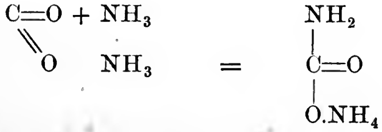
which is capable of further direct combination with other elements. By union with oxygen it forms carbonic anhydride, $\mathrm{C}\begin{smallmatrix}\diagup\!\!\diagup\mathrm{O}\\\diagdown\!\!\diagdown\mathrm{O}\end{smallmatrix}$; it unites with nascent chlorine, or with chlorine gas in sunlight, to form carbonic oxychloride, or phosgene gas:



The latter compound, formerly only known in the gaseous state, has lately been obtained, by sufficient reduction of temperature, as a colourless liquid of specific gravity 1·432, and boiling at + 8°. The liquid is most readily obtained when chloroform (two parts) is heated with a mixture of potassic dichromate (five parts) and sulphuric acid (forty parts), and the evolved gases conducted through strongly cooled tubes.

The properties and modes of preparation of the oxides and sulphides of carbon and of the metallic carbonates will not be referred to here, being fully described in works on inorganic chemistry. The amide derivatives of carboxyl require considerable notice.

129. *Carbamic Acid.*—The white powder, obtained by mixing ammonia with carbonic anhydride, in absence of water, formerly regarded as anhydrous ammonic carbonate, is the ammonic salt of carbamic acid:



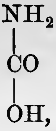
It is usually prepared by passing the two dry gases into absolute alcohol, from which it separates slowly in thin leafy crystals. It sublimes below 100°, and unites with water to form ammonic carbonate:

$$CO.NH_2.ONH_4 + H_2O = CO(ONH_4)_2;$$

from which it can in part be again obtained by sublimation:

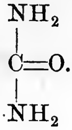
$$CO(ONH_4)_2 = H_2O + CO.NH_2.ONH_4;$$

so that the ammonic carbonate of commerce invariably contains small quantities of this salt.

Carbamic acid,  $\begin{array}{l}NH_2\\ |\\ CO\\ |\\ OH,\end{array}$ cannot be obtained from its salts by action of acids, carbonic anhydride and ammonia being formed. It is more stable in its ethers, i.e. those compounds which contain an alcohol residue, instead of the hydroxyl-hydrogen atoms, and which are termed *urethanes*; they will be found described under the respective alcohols.

Carboxylimid, $C{\ll}^{O}_{N-H}$: see pseudocyanic acid (§ 100).

Urea.

130. *Carboxyldiamine, carbamide,* CH_4N_2O =  $\begin{array}{l}NH_2\\ |\\ C{=}O.\\ |\\ NH_2\end{array}$ Urea occurs in the urine of all animals, more especially of the mammalia, and amongst these in largest quantity in that of carnivoræ; also in other animal fluids, as in blood, the amniotic liquid, and the vitreous humour of the eyes of mammalia, &c., but normally in only small quantity. In animal bodies, it results from the retrograde metamorphosis of nitrogenous tissue, and also from the direct decomposition of nitrogenous food without previous conversion into animal tissue. It is separated from the blood by the kidneys, and leaves the body in the urine. On interruption of the secretion by the kidneys, its quantity increases in the blood and other animal fluids.

It is prepared synthetically (together with other bodies) by action of ammonia upon carbonic oxychloride:

$$COCl_2 + 4NH_3 = 2NH_4Cl + CO(NH_2)_2,$$

on carbonic ethers and urethanes. It is further formed from cyanamide on treatment with dilute nitric acid (§ 114), most easily by the transformation of ammonic cyanate (§ 103).

This last method of preparation was discovered by Wöhler in 1828, and is historically important, as the first instance of an undoubtedly organic body being obtained by artificial means.

Instead of preparing ammonic cyanate from cyanic acid and ammonia gas, and then transforming it into urea by repeated solution in water and evaporation, the aqueous solution of crude potassic pseudocyanate is decomposed by an equivalent quantity of ammonic sulphate:

$$2C{\ll}^{O}_{N-K} + (NH_4)_2SO_4 = 2C{\ll}^{O}_{N-NH_4} + K_2SO_4.$$

whereby, instead of ammonic pseudocyanate, urea is obtained:

$$C{\ll}^{O}_{N-NH_4} = C\begin{cases}{=}O\\ {-}NH_2\\ {-}NH_2\end{cases}$$

The liquid is then concentrated on the water bath, by which means the greater part of the potassic sulphate separates, and can be filtered off; the mother liquor is then evaporated to dryness, and the urea extracted from the residue by absolute alcohol, potassic sulphate being completely insoluble.

Urea can be obtained with equal ease from human urine. The urine is evaporated on the water bath to a syrupy consistence, then cooled with slow addition of excess of nitric acid, whereupon the whole solidifies to a pasty mass of urea nitrate; this is freed from the mother liquor by draining and pressure between porous plates, and recrystallised from lukewarm water. It is then usually treated with animal charcoal, to remove colouring matters as far as possible. The purified nitrate is then dissolved in warm water, decomposed with baric carbonate:

$$2CO(NH_2)_2.HNO_3 + BaCO_3 = Ba(NO_3)_2 + CO_2 + H_2O + 2CO(NH_2)_2,$$

the whole evaporated to dryness on the water bath, and the free urea dissolved by strong boiling alcohol, in which baric nitrate is insoluble.

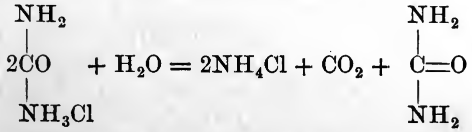
131. Urea crystallises in long colourless prisms, of neutral reaction, destitute of odour, and of cooling nitre-like taste. It melts at 130° and decomposes at a slightly higher temperature, with evolution of ammonia.

It is extremely soluble in water, and in boiling absolute alcohol. It requires for solution five times its weight of cold alcohol, and is nearly completely insoluble in ether.

132. *Compounds of Urea with Acids.*—Urea behaves towards acids like a weak basic amide, i.e. it forms salts with them, similar to those of ammonia; although derived from two molecules of the latter, it however only combines with one molecule of a monobasic acid. The amide derivatives of organic acids, to be described further on, in which the carboxyl group is united with a single amide group, show little or no disposition to unite with acids, so that the electro-negative radical CO greatly hinders or entirely removes the disposition of the nitrogen to combine with acids.

A similar influence is exerted by carboxyl on the two amide groups combined with it in urea, so much so that the union of one amide group with an acid is sufficient to destroy the basic character of the whole molecule.

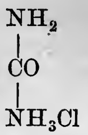
All salts of urea show an acid reaction, and a strong tendency to decompose in aqueous solution; there results from their decomposition ammonic salts, carbonic anhydride, and urea:



$$2\begin{array}{c}NH_2\\|\\CO\\|\\NH_3Cl\end{array} + H_2O = 2NH_4Cl + CO_2 + \begin{array}{c}NH_2\\|\\C{=}O\\|\\NH_2\end{array}$$

In preparing urea salts, therefore, the presence of water must either be entirely avoided, or at least any warming therewith, as this materially assists the decomposition. Of these salts the following are noteworthy:

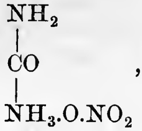
Urea hydrochloride, $CON_2H_4.HCl =$



$$\begin{array}{c}NH_2\\ |\\ CO\\ |\\ NH_3Cl\end{array}$$

, obtained by action of dry hydrochloric acid gas on urea, with considerable evolution of heat, as a thick liquid, which forms a crystalline mass on cooling; it is extremely soluble in water, and deliquesces in moist air with very ready decomposition.

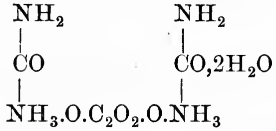
Urea nitrate, $CON_2H_4.HNO_3 =$



$$\begin{array}{c}NH_2\\ |\\ CO\\ |\\ NH_3.O.NO_2\end{array}$$

, separates from urea solutions on addition of nitric acid, in white masses, which are pretty soluble in water, but very difficultly soluble in dilute nitric acid. On heating to 150° it decomposes suddenly with violent evolution of gas.

Urea oxalate, $2CON_2H_4,H_2C_2O_4,2H_2O$

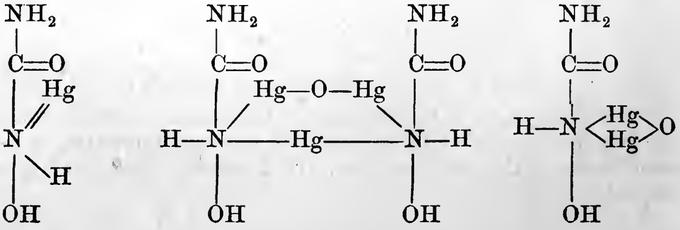


$$= \begin{array}{ccc}NH_2 & & NH_2\\ | & & |\\ CO & & CO,2H_2O\\ | & & |\\ NH_3 & .O.C_2O_2.O. & NH_3\end{array}$$

is precipitated, by addition of oxalic acid to moderately concentrated solutions of urea, in long thin leaves, which are difficultly soluble in cold water.

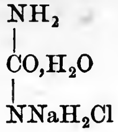
133. *Compounds of Urea with Metallic Oxides.*—Urea forms crystalline compounds with the oxides of mercury and silver. Both metals very easily replace a portion of the hydrogen in ammonia by action of their oxides upon it, and their behaviour with organic amide compounds is similar; it is therefore most probable that in the above-mentioned compounds the metal is in direct union with nitrogen.

Urea mercuric oxide is formed directly by digesting a solution of urea with mercuric oxide, as a white crystalline powder of the formula CON_2H_4,HgO. Another compound, $2CON_2H_4,3HgO$, results, by mixing an alkaline solution of urea with mercuric chloride, as a gelatinous precipitate, which becomes granular in hot water, whilst mercuric nitrate, similarly heated, gives a body of the formula $CON_2H_4,2HgO$. The constitution of these compounds may be expressed by the structural formulæ



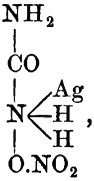
Urea argentic oxide, $2CON_2H_4,3Ag_2O$, separates as a granular grey powder; when freshly precipitated argentic oxide is left for some time at 40°–50° in contact with urea solution.

134. *Compounds of Urea with Salts.*—The methods of combination occurring in the compounds formed by union of urea with acids and with oxides respectively, both occur in its union with many salts. These bodies are obtained by evaporating the mixed solutions of their components.

Urea sodic chloride, $CON_2H_4,NaCl,H_2O$, probably 

$$\begin{array}{l} NH_2 \\ | \\ CO,H_2O \\ | \\ NNaH_2Cl \end{array}$$

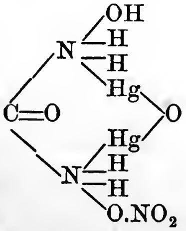
separates in large coloured crystals on evaporating human urine, in colourless shining prisms on adding the requisite amount of common salt to pure urea solution. The presence of a small quantity of this compound in a solution of a large quantity of common salt, causes this latter to separate in octahedra on evaporation.

Urea argento-nitrate, $CON_2H_4,AgNO_3$ = , separates, on mixing concentrated solutions of its components, in large rhombic prisms.

$$\begin{array}{l} NH_2 \\ | \\ CO \\ | \\ N{\begin{array}{l} Ag \\ H \\ H \end{array}} \\ | \\ O.NO_2 \end{array}$$

Urea unites in a similar manner with the nitrates of sodium, calcium, magnesium, &c.

On mixing urea solution with mercuric nitrate, there results a snow-white flocculent precipitate of varying composition, according to the concentration of the mixed liquids, &c. These precipitates contain urea, nitric acid, and the elements of mercuric oxide, the latter being in excess. With very dilute solutions, the compound precipitated has the empirical formula $CON_2H_4,2HgO,HNO_3$;

probably 

135. *Estimation of Urea by Titration.*—Liebig devised a method for the estimatiom of urea, based on the formation of the above-mentioned compound, which, whilst sufficiently accurate for most purposes, has the advantages of quickness and simplicity.

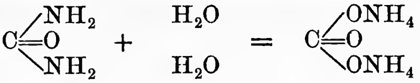
A solution of mercuric nitrate is prepared which contains 71·48 grams of mercury per litre. One c.c. of this solution is sufficient to precipitate ·01 gram of urea from a two per cent. solution. In the reaction that ensues on adding the standard mercury solution to the urea, nitric acid is set free, and as the precipitate is soluble to a considerable extent in this, the end of the reaction cannot be arrived at by adding the mercury solution until no more precipitate is formed. By taking small portions of the liquid out from time to time during the titration, and testing them with sodic hydrate, the end point is easily seen, as a yellow precipitate of mercuric oxide results as soon as the mercury solution is in the least excess, instead of the white precipitate previously obtained. The number of c.c. of mercuric nitrate solution required to arrive at this point, multiplied by ·01, gives the weight of urea present.

In the estimation of urea in urine, the phosphoric acid present must be previously removed; this is best done by adding excess of a mixture of baric hydrate and nitrate (both this and the urea solutions being measured); the resulting precipitate is then removed by means of an unmoistened filter and the filtrate then titrated.

As urine always contains sodic chloride, and this latter converts the mercury solution into mercuric chloride, which gives no precipitate with urea in non-alkaline solutions, the free baric hydrate is neutralised, and mercury solution run in until a cloudiness is produced, which remains after vigorous shaking; this indicates that all the sodic chloride has been decomposed, and the burettes can now be read off, and the titration proceeded with as above.

136. *Decompositions of Urea.*—Of the numerous decompositions of urea, the following are the most important.

Urea unites with the elements of two molecules of water to form ammonic carbonate:



$$C\begin{cases}NH_2\\ O\\ NH_2\end{cases} + \begin{matrix}H_2O\\ \\ H_2O\end{matrix} = C\begin{cases}ONH_4\\ O\\ ONH_4\end{cases}$$

At ordinary temperatures this decomposition only takes place with the aid of ferments, as, for instance, in the alkaline putrefaction of urine; by boiling in aqueous solution it occurs only slowly, more quickly by heating in sealed tubes to 230°–240°.

Urea suffers analogous decompositions when heated with strong acids and alkalies; in the first case, carbonic anhydride and the ammonic salts of the respective acids are formed:

$$CO(NH_2) + H_2O + 2H_2SO_4 = 2(NH_4)HSO_4 + CO_2 ;$$

in the second case, carbonate of the alkali and free ammonia:

$$CO(NH_2)_2 + 2KOH = CO(OK)_2 + 2NH_3.$$

Methods for the estimation of urea are similarly founded on those reactions; either it is decomposed by concentrated sulphuric acid, and the amount of ammonia combined with the latter determined, or it is heated with baric hydrate to a high temperature, and the baric carbonate weighed:

$$CO(NH_2)_2 + Ba(OH)_2 = BaCO_3 + 2NH_3.$$

By heating with argentic nitrate, argentic pseudocyanate and ammonic nitrate are formed:

$$CO(NH_2)_2 + AgNO_3 = CO.NAg + NH_4.NO_3.$$

Urea is also converted into cyanogen derivatives when heated by itself; at 150°–160° ammonia is evolved, at first with incipient fusion of the mass, which then solidifies and consists of cyanuric acid (§ 104), ammelide, or cyameluric acid and biuret (§ 137). This decomposition is represented by the equations:

$$3CON_2H_4 = 3NH_3 + (C_3N_3)\,(OH)_3 \text{ (cyanuric acid).}$$
$$3CON_2H_4 = 2NH_3 + H_2O + (C_3\dot{N}_3)\left\{\begin{matrix}(OH)_2\\ NH_2\end{matrix}\right. \text{ (ammelide).}$$
$$2CON_2H_4 = NH_3 + C_2O_2N_3H_5 \text{ (biuret).}$$

The first of these is the reversal of the formation of urea from ammonic cyanate.

Cyanuric acid alone is obtained by heating urea hydrochloride to a high temperature:

$$3CO(NH_2).(NH_3Cl) = 3NH_4Cl + (C_3N_3)\,(OH)_3.$$

Chlorine gas acts similarly when passed over fused urea, but nitrogen and hydrochloric acid are also formed:

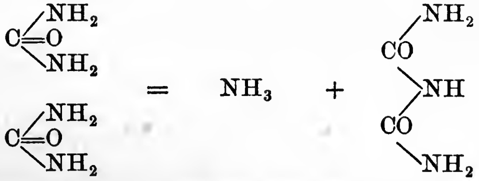
$$6CON_2H_4 + 3Cl_2 = 2C_3N_3O_3H_3 + 4NH_4Cl + 2HCl + N_2.$$

By the dry distillation of urea with phosphoric anhydride, cyanic acid distils over, whilst ammonic metaphosphate and ammelide remain behind.

Dicyandiamidine (§ 116) is probably urea-guanidine.

Biuret.

137. *Dicarboxyl-diamid-imide*, $C_2O_2N_3H_5$, has already been mentioned above as one of the decomposition-products of urea, when heated to 150°–160°. It is obtained from two molecules of the latter, one losing an amide group, and the other a hydrogen atom, the bonds thereby set free uniting:



Biuret is extracted from the solidified residue by cold water, the small quantity of cyanuric acid dissolved, precipitated by plumbic acetate, and any excess of lead removed from the solution by hydric sulphide; the clear solution yields, by evaporation, biuret in pretty soluble colourless needles containing one molecule of water of crystallisation; this latter is removed on exposure to dry air.

A characteristic reaction of biuret is its power, in presence of alkalies, of dissolving cupric oxide to a reddish-violet solution; the copper without doubt replacing some of the hydrogen of the biuret.

On mixing a solution of biuret with argentic nitrate, and then carefully adding alkali, a colourless but easily blackened precipitate of *diargento-biuret*, $C_2O_2N_3H_3Ag_2$, is obtained.

Anhydrous biuret melts at 190°, and at a slightly higher temperature decomposes into cyanuric acid and ammonia:

$$3C_2O_2N_3H_5 = 3NH_3 + 2C_3N_3H_3O_3.$$

Heated to 100° in an atmosphere of hydrochloric acid, it yields a saline compound of the formula $2C_2O_2N_3H_5,HCl$; at higher temperatures it gives guanidine hydrochloride, and carbonic anhydride:

$$C_2O_2N_3H_5 + HCl = CO_2 + CN_3H_5.HCl,$$

together with sal ammoniac and a difficultly soluble compound, which has been termed urea-cyanurate:

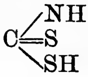
$$2C_2O_2N_3H_5 + HCl = NH_4Cl + C_4H_7N_5O_4.$$

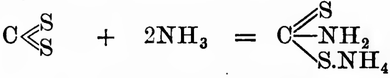
This latter is probably a body of analogous composition to biuret, and may be viewed as tetruret:

$$\begin{array}{ll} NH_2.CO.NH.CO.NH_2 & \text{(biuret).} \\ NH_2.CO.NH.CO.NH.CO.NH.CO.NH_2 & \text{(tetruret).} \end{array}$$

The relations of biuret to the so-called allophanic ethers will be spoken of later.

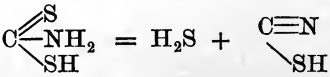
138. Corresponding to carboxyl is the radical CS, thiocarbonyl, which has, however, as yet never been obtained uncombined like carbonic oxide; it has only to be mentioned here in connection with its amide derivatives, which in their behaviour closely resemble the carboxylamide compounds.

139. *Sulpho-carbamic acid*, CH_3NS_2 =  $C\left\{\begin{array}{l} NH_2 \\ =S \\ SH \end{array}\right.$, ammonic sulpho-carbamate, is formed (like the corresponding oxy-derivative) by action of ammonia on carbonic disulphide, best when alcoholic solutions of both are employed:



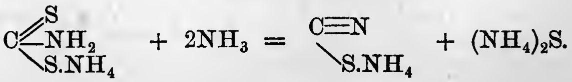
$$C\begin{array}{l} =S \\ =S \end{array} + 2NH_3 = C\left\{\begin{array}{l} =S \\ NH_2 \\ S.NH_4 \end{array}\right.$$

From this salt, which crystallises in yellow prisms, sulpho-carbamic acid is obtained, by action of hydrochloric acid, as a reddish-coloured oily liquid, which solidifies at ordinary temperatures to a crystalline mass, and after a time decomposes spontaneously into sulpho-cyanic acid and hydric sulphide:



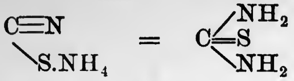
$$C\left\{\begin{array}{l} =S \\ NH_2 \\ SH \end{array}\right. = H_2S + \begin{array}{l} C\equiv N \\ \diagdown SH \end{array}$$

By heating with excess of ammonia, ammonic sulpho-carbamate is converted into ammonic sulpho-cyanate:



$$C\left\{\begin{array}{l} =S \\ NH_2 \\ S.NH_4 \end{array}\right. + 2NH_3 = \begin{array}{l} C\equiv N \\ \diagdown S.NH_4 \end{array} + (NH_4)_2S.$$

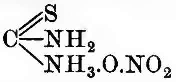
140. *Sulphurea,* or *sulpho-carbonyl diamide,* CSN_2H_4. Whilst ammonic cyanate changes at ordinary temperatures into urea, ammonic sulpho-cyanate only undergoes the same change at higher temperatures:



$$\begin{matrix} C\equiv N \\ \quad \diagdown S.NH_4 \end{matrix} = C\begin{matrix} \diagup NH_2 \\ = S \\ \diagdown NH_2 \end{matrix}$$

In order to prepare sulphurea, dry ammonic sulpho-cyanate is heated slowly to 170°, and kept at that temperature for several hours; it is then cooled to 100°, and dissolved in an equal weight of water at 80°, filtered and cooled to crystallisation. The crystals are freed from the mother liquor, which contains unaltered ammonic sulpho-cyanate, and purified by repeated recrystallisation from very little hot water. Sulphurea crystallises in prisms, dissolves readily in water and alcohol, but little in ether, and fuses at 149°.

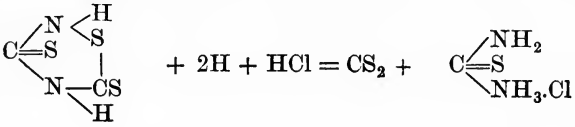
Like urea, it yields with nitric acid a difficultly soluble nitrate:



$$C\begin{matrix} \diagup\!\!\diagup S \\ - NH_2 \\ \diagdown NH_3.O.NO_2 \end{matrix}$$

Argentic and mercuric derivatives are also known, which decompose readily with formation of metallic sulphides. Similarly also on boiling its aqueous solution with argentic or mercuric oxides, the respective metallic sulphides are precipitated, whilst dicyandiamide remains in solution. By heating with water it is reconverted into ammonic sulpho-cyanate.

Hydro-halogen derivatives of sulphurea are formed easily, together with carbonic disulphide, by simultaneous action of nascent hydrogen and hydro-haloids upon persulpho-dicyanic acid:



ETHANES OR PARAFFINS.

HYDROCARBONS OF THE SERIES C_nH_{2n+2}.

141. The homologous series of paraffins embraces those hydrocarbons in which the maximum possible number of hydrogen atoms is attached to the carbon nucleus (§ 40.) Its first member is marsh gas or methane, CH_4, from which the higher members of the series can be obtained by substitution of its hydrogen by the hydrocarbon radicals of the series C_nH_{2n+1} :

$$\begin{aligned}
CH_4 - H + C_nH_{2n+1} &= CH_3 \,.\, C_nH_{2n+1} &&= C_{(n+1)}\, H_{2(n+1)+2} \\
CH_4 - 2\,H + 2\,C_nH_{2n+1} &= CH_2 \,.\, (C_nH_{2n+1})_2 &&= C_{(2n+1)}\, H_{2(2n+1)+2} \\
CH_4 - 3\,H + 3\,C_nH_{2n+1} &= CH\ (C_nH_{2n+1})_3 &&= C_{(3n+1)}\, H_{2(3n+1)+2} \\
CH_4 - 4\,H + 4\,C_nH_{2n+1} &= C\ (C_nH_{2n+1})_4 &&= C_{(4n+1)}\, H_{2(4n+1)+2}
\end{aligned}$$

The series is therefore also known as the marsh gas series.

The first three members (CH_4, C_2H_6, and C_3H_8) each exist in only a single modification; those richer in carbon show isomers, the possible number of which increases with the carbon contents of each member, and is equal to the number of possibilities of structure in the nucleus, only nucleus-isomerism (§ 46) being possible.

The hydrogen atoms of the paraffins can be replaced in different amounts, partly directly, as by the halogens, partly indirectly by other elements or radicals. There thereby results an enormous number of organic bodies which are known as the marsh gas derivatives, and which in their totality are known as fatty compounds.

The unattacked remaining hydrocarbon residues of increasing valency :

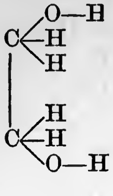
$$C_nH_{2n+1}\,;\ C_nH_{2n}\,;\ C_nH_{2n-1}\,;\ C_nH_{2n-2}\,;\ C_nH_{2n-3}\,;\ C_nH_{2n-4},\ \&c.,$$

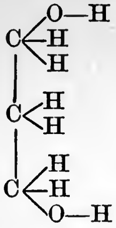
remain as radicals, and are named after their simplest oxides, which are the oxygen substitution-derivatives of the paraffins.

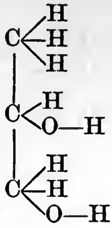
142. By substitution of only a single hydrogen atom in a paraffin, a residue of the formula C_nH_{2n+1} remains, which exists in combination with the substituting element or compound radical. Is this latter hydroxyl there results the hydrate of the residue, which is termed a *monacid alcohol.* The residue itself is termed an alcohol radical or *alkyl.*

143. If substitution of two hydrogen atoms occurs in a paraffin, it can be either at two carbon atoms—one at each—or at one single primary or secondarily combined carbon atom of the nucleus.

In the first case there results, if hydroxyl be the substituting radical, the so-called *diacid alcohols*, or *glycols* :

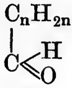






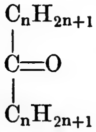
On the other hand, if the substitution of two hydrogen atoms be at a single carbon atom, there results, if this is

a. A terminal carbon atom, the compounds of the *aldehyde radicals*, so-named from their oxides the aldehydes :



$$\begin{matrix} C_nH_{2n+1} \\ | \\ C{<}^{H}_{O} \end{matrix} \quad \text{or} \quad C_{(n+1)}H_{2(n+1)}O \quad \text{or} \quad C_{n'}H_{2n'}O, \text{ if } _{n+1} = _{n'}.$$

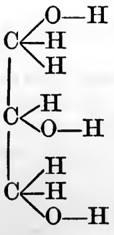
b. If, on the contrary, the substitution be at a secondarily combined, intermediate carbon atom, the residue C_nH_{2n} is termed a ketone radical, as the oxides are termed *ketones* :



$$\begin{matrix} C_nH_{2n+1} \\ | \\ C{=}O \\ | \\ C_nH_{2n+1} \end{matrix} \quad = C_{(2n+1)}H_{2(2n+1)}O \text{ or } C_{n'}H_{2n'}O, \text{ if } _{2n+1} = _{n'}.$$

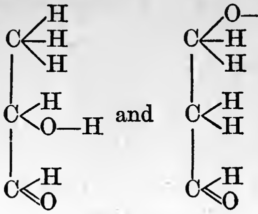
144. When three hydrogen atoms in a paraffin are replaced by other elements the complication is greatly increased. On a nucleus containing at least three carbon atoms, each hydrogen atom may be substituted on a different carbon atom; the resulting residue is the radical of the trivalent alcohols or glycerines, that being the name by which their hydrates are distinguished :

Glycerine

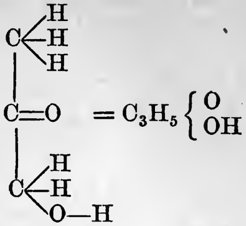


$= C_3H_5(OH)_3$

If the substitution takes place at two different carbon atoms—i.e. at one a single, at a second a double substitution—there must result oxides which combine the characters of alcohols with those of aldehydes or ketones; e.g.



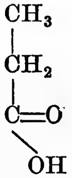
Aldehyde alcohols.



$= C_3H_5\left\{\begin{matrix}O\\OH\end{matrix}\right.$

Ketone alcohol.

Triple substitution can only take place at a single carbon atom, if the latter be at the end of a chain; the simplest oxides of the residues have then the characters of acids:



145. The more hydrogen atoms there are replaced in a paraffin the more numerous must be the resulting products. But as, with exception of marsh gas, the series never contains carbon atoms united with more than three hydrogen atoms, there results, from a greater substitution than three, only combinations of the simpler categories, and there are obtained every time:

1. By replacement of only one hydrogen atom at a carbon atom, by OH, an alcohol, or alcohol derivative, if other elements or compound radicals are the replacing bodies. The number of these varieties of substitution that can take place in a paraffin expresses the valency of the alcohol radical, or the 'acidity' of the alcohol. It results from this that an *x* acid alcohol must contain at least *x* carbon atoms in its nucleus.

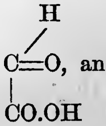
2. By simultaneous replacement of two hydrogen atoms united to one and the same carbon atom, there are obtained:

   a. If the replacement be at a terminal carbon atom: aldehydes or aldehyde derivatives.

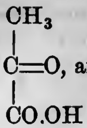
   b. If at an intermediate carbon atom: ketones or ketone derivatives.

3. Organic acids (in the true sense) or their derivatives are formed when the three hydrogen atoms attached to a terminal carbon atom are simultaneously replaced.

As ketone alcohols and aldehyde alcohols are known, so similarly there are alcohol acids, i.e. $\begin{matrix}CH_2.OH\\ |\\ CO.OH\end{matrix}$, aldehyde acids,



$\begin{matrix}H\\ /\\ C{=}O\\ |\\ CO.OH\end{matrix}$

, and ketonic acids,  $\begin{array}{c} CH_3 \\ | \\ C{=}O \\ | \\ CO.OH \end{array}$, and many similar complications, which with some less known categories of transformation and substitution-derivatives of the paraffins will be mentioned at their respective places.

146. The series of paraffins contains members with nuclei of from one to at least thirty atoms of carbon, and their isomers. Those poorest in carbon are gases; by increasing carbon contents liquids and solids follow, whose boiling and melting points increase, as a rule, with the increase in molecular weight. They are nearly or quite insoluble in water, burn easily when heated in an oxygen-containing atmosphere, and are converted into substitution-derivatives by the action of the halogens—especially chlorine—when exposed to light or heat:

$$C_nH_{2n+2} + Cl_2 = HCl + C_nH_{2n+1}Cl$$
$$C_nH_{2n+2} + 2Cl_2 = 2HCl + C_nH_{2n}Cl_2$$
$$C_nH_{2n+2} + 3Cl_2 = 3HCl + C_nH_{2n-1}Cl_3 \qquad \&c.$$

Many paraffins are also attacked by strong nitric acid, water being eliminated, and a product formed which contains the nitric acid radical NO_2 (nitryl) in place of hydrogen. Such bodies are termed nitro-paraffins. The paraffins are very indifferent to most reagents.

Occurrence and Formation of the Paraffins.

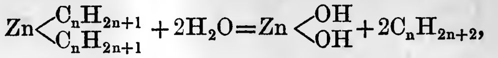
147. Many hydrocarbons of the marsh-gas series occur ready-formed in nature; they are formed mostly by the decomposition of dead putrefying or decaying organisms, and are therefore very frequently found with coal. The liquid and solid paraffins form the chief proportion of mineral oil or petroleum, from which a large number of members of the series have been isolated by fractional distillation.

Paraffins are also formed in the dry distillation of many organic bodies, though, with the exception of the gaseous members, only in small quantity and varying proportion. The latter depends on the temperature employed and the duration of the heating, and cannot at present be deduced into a rule approaching certainty. On the other hand, a series of reactions are known which serve for the preparation of individual members of the series.

148. *Synthetical Methods of Preparing Paraffins.*—No paraffin has been prepared as yet by the direct action of carbon upon hydrogen; marsh gas, however, has been obtained by means of very simple mineral compounds (see later). The above-mentioned methods of the synthesis of paraffins are from already existing organic bodies, and fall into two groups, accordingly as the transformation takes place on already existing carbon nuclei, without increase thereof, or by the synthetical formation of the nucleus by combination of simpler carbon nuclei, this latter being known as nucleus-synthesis. Of both methods the following may be mentioned as the most important.

149. *Methods without Increase of Nucleus.*—These consist without exception in joining the maximum number of hydrogen atoms to the nucleus chosen.

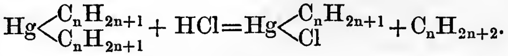
For such methods the zinc compounds of the monovalent alcohol radicals are most particularly available. They react with water, according to the equation



$$Zn{<}\begin{matrix}C_nH_{2n+1}\\ C_nH_{2n+1}\end{matrix} + 2H_2O = Zn{<}\begin{matrix}OH\\ OH\end{matrix} + 2C_nH_{2n+2},$$

with such violence that explosions will ensue unless the ingredients are mixed with great care—best previously diluted with indifferent liquids.

Other organo-metallic bodies, such as those of mercury, may be employed, but halogen acids must then be used in place of water, this latter not altering them:



$$Hg{<}\begin{matrix}C_nH_{2n+1}\\ C_nH_{2n+1}\end{matrix} + HCl = Hg{<}\begin{matrix}C_nH_{2n+1}\\ Cl\end{matrix} + C_nH_{2n+2}.$$

The halogen atoms in the haloid salts of the mono- and polyvalent alcohol radicals can be substituted by hydrogen in various ways, as by action of zinc and hydrochloric acid in alcoholic solution:

$$C_nH_{2n+1}Cl + Zn + HCl = C_nH_{2n+2} + ZnCl_2.$$

The iodides of the alcohol radicals suffer such decomposition most readily. They are decomposed by heating with zinc and water to about 200°:

$$2C_nH_{2n+1}I + 2Zn + 2OH_2 = Zn(OH)_2 + ZnI_2 + 2C_nH_{2n+2};$$

as also by long heating with concentrated hydriodic acid to 200°–300°:

$$C_nH_{2n+1}I + HI = C_nH_{2n+2} + I_2$$
$$C_nH_{2n}I_2 + 2HI = C_nH_{2n+2} + 2I_2.$$

Instead of first preparing the iodide from the alcohol, the latter can be decomposed directly by hydriodic acid:

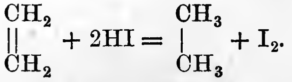
$$C_nH_{2n+1}OH + 2HI = C_nH_{2n+2} + OH_2 + I_2.$$

It appears generally that by action of saturated hydriodic acid solution, all organic oxides are converted into the corresponding paraffins:

$$C_2H_4O + 4HI = C_2H_6 + H_2O + 2I_2$$
$$C_2H_4O_2 + 6HI = C_2H_6 + 2H_2O + 3I_2.$$

By most of the methods previously mentioned the paraffins are formed as the hydrides of the alcohol radicals, and they are frequently referred to as such.

The unsaturated hydrocarbons are also converted into paraffins by hydriodic acid, hydrogen being taken up and iodine separated:

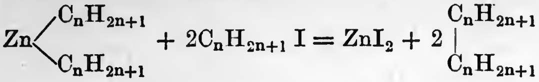


$$\begin{matrix}CH_2\\ \|\\ CH_2\end{matrix} + 2HI = \begin{matrix}CH_3\\ |\\ CH_3\end{matrix} + I_2.$$

The salts of organic acids yield paraffins when fused with alkalies, with partial splitting off of carbon as carbonate:

$$C_nH_{2n+1}.CO.OK + HOK = K_2CO_3 + C_nH_{2n+2},$$
$$C_nH_{2n}(CO.OK)_2 + 2HOK = 2K_2CO_3 + C_nH_{2n+2}, \&c.$$

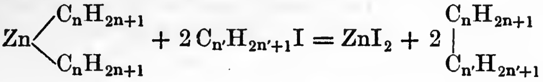
150. *Methods with Synthesis of Carbon Nuclei.*—These consist without exception of methods in which the elements in combination with hydrocarbon nuclei are withdrawn by substances having a stronger affinity for them, whereupon the several hydrocarbon nuclei unite at the moment of liberation and form new molecules. The general type of reaction thus occurring is that known as double decomposition, as by action of the iodides of the alcohol radicals upon the corresponding zinc compounds :



$$\mathrm{Zn}\begin{matrix}\diagup C_nH_{2n+1}\\ \diagdown C_nH_{2n+1}\end{matrix} + 2C_nH_{2n+1}\,I = ZnI_2 + 2\begin{matrix}C_nH_{2n+1}\\ |\\ C_nH_{2n+1}\end{matrix}$$

$$= 2C_{2n}H_{4n+2} \text{ or } C_mH_{2m+2}, \text{ if } {}_{2n} = {}_{m},$$

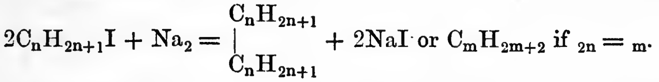
or by the employment of the zinc compound of one radical with the iodide of another :



$$\mathrm{Zn}\begin{matrix}\diagup C_nH_{2n+1}\\ \diagdown C_nH_{2n+1}\end{matrix} + 2\,C_{n'}H_{2n'+1}I = ZnI_2 + 2\begin{matrix}C_nH_{2n+1}\\ |\\ C_{n'}H_{2n'+1}\end{matrix}$$

$$= 2C_{n+n'}H_{2n+2n'+2} = C_mH_{2m+2}, \text{ if } {}_{m} = {}_{n} + {}_{n'}.$$

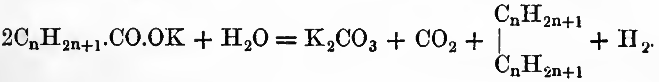
A similar result is obtained when the iodide or bromide of an alcohol radical, dissolved in an indifferent liquid—ether, &c.—is heated with potassium or sodium :



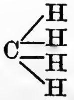
$$2C_nH_{2n+1}I + Na_2 = \begin{matrix}C_nH_{2n+1}\\ |\\ C_nH_{2n+1}\end{matrix} + 2NaI \text{ or } C_mH_{2m+2} \text{ if } {}_{2n} = {}_{m}.$$

When obtained by the last two methods the paraffins appear as the compounds of two similar or different alcohol radicals.

Another method belonging to this class is the decomposition of aqueous solutions of salts of organic acids by the electric current, whereby carbonic anhydride and the paraffin appear at the positive pole, and hydrogen and solution of the carbonate at the negative :



$$2C_nH_{2n+1}.CO.OK + H_2O = K_2CO_3 + CO_2 + \begin{matrix}C_nH_{2n+1}\\ |\\ C_nH_{2n+1}\end{matrix} + H_2.$$

Methane, CH_4 or 

(Methylic hydride, carbonic tetrahydride.)

151. Methane is invariably formed by the spontaneous decomposition of organic bodies out of contact with air, i.e. during their putrefaction, and therefore occurs in the slime of marshy waters in large quantity (marsh gas), very frequently in coal mines (fire-damp.) At some places it streams in large quantity from the ground—e.g. at Baku on the Caspian Sea, where it has burnt since a very remote period.

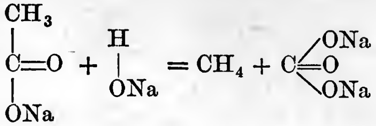
Mixed with other hydrocarbons it is formed by the dry distillation of most organic bodies, and therefore occurs in coal gas.

To prepare perfectly pure methane, zinc methyl is decomposed by water :

$$Zn(CH_3)_2 + 2H_2O = Zn(OH)_2 + 2CH_3.H \text{ or } 2CH_4.$$

Methylic hydride.

It is obtained nearly pure when an intimate mixture of sodic acetate with double its weight of soda lime is heated strongly :



$$CH_3{-}C({=}O){-}ONa + H{-}ONa = CH_4 + C({=}O)(ONa)_2$$

It can be prepared indirectly from its elements in two ways—either by passing a mixture of sulphuretted hydrogen and carbonic disulphide vapour over glowing copper, which removes the sulphur from both compounds :

$$CS_2 + 2SH_2 + 8Cu = 4Cu_2S + CH_4 ;$$

or by action of sodium amalgam on carbonic tetrachloride in presence of water :

$$CCl_4 + 4Na_2 + 4OH_2 = 4NaCl + 4NaOH + CH_4.$$

Methane is a colourless, odourless gas of sp. gr. ·5598 ; it is slightly absorbed by water. It burns readily with a feebly luminous flame ; mixed with the requisite quantity of oxygen (double its volume) or atmospheric air, it explodes on ignition with great violence (fire-damp) :

$$CH_4 + 2O_2 = CO_2 + 2OH_2.$$

Although it does not support respiration, it is destitute of poisonous qualities. Under the influence of high temperatures—e.g. when passed through white-hot porcelain tubes, or when submitted for a long time to the action of the electric spark—it is partly decomposed, with increase of volume, into hydrogen and carbon :

$$CH_4 = C + 2H_2.$$

When mixed in the dry state with chlorine, it is not affected in the dark ; by heating, however, or by exposure to light, it undergoes changes whose amount depends upon that of the chlorine present.

A mixture of one volume of methane with two volumes of chlorine explodes powerfully on exposure to direct sunlight, carbon being deposited, and hydrochloric acid gas formed :

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

If the gases be mixed in equal volumes, and exposed to diffused daylight, substitution of one hydrogen by one chlorine atom takes place, and monochlor-methane or methylic chloride results :

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

Larger quantities of chlorine by slow action—best and with least danger if diluted with large quantities of carbonic anhydride—yield higher chlorine substitution-products:

$$CH_4 + 2Cl_2 = 2HCl + CH_2Cl_2$$ (dichlor-methane, or methylene dichloride),

$$CH_4 + 3Cl_2 = 3HCl + CHCl_3$$ (trichlor-methane, or chloroform),

and lastly

$$CH_4 + 4Cl_2 = 4HCl + CCl_4$$ (tetrachlor-methane, perchlor-methane, or carbonic chloride).

In the presence of water, chlorine decomposes methane, slowly but completely, into hydrochloric acid and carbonic anhydride:

$$CH_4 + 2H_2O + 4Cl_2 = 8HCl + CO_2.$$

Ethane, C_2H_6.

(Ethylic hydride, C_2H_5H. Dimethyl, $\begin{array}{l}CH_3\\ | \\ CH_3\end{array}$)

152. Ethane is obtained, as ethylic hydride, from zinc ethyl and water:

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

by heating ethylic iodide with zinc and water to 150°:

$$2C_2H_5I + 2Zn + H_2O = ZnI_2 + ZnO + 2C_2H_6;$$

and by action of strong hydriodic acid upon ethylic iodide under the influence of high temperatures:

$$C_2H_5I + HI = C_2H_6 + I_2.$$

From hydrocarbons poorer in hydrogen, as from ethylene (C_2H_4) and acetylene (C_2H_2), it is obtained by the same reagent at 250°:

$$C_2H_4 + 2HI = C_2H_6 + I_2$$
$$C_2H_2 + 4HI = C_2H_6 + 2I_2.$$

As dimethyl it is formed by heating methylic iodide with zinc or molecular silver in closed tubes at 150°:

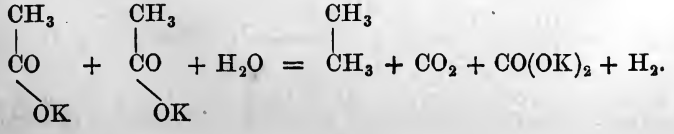
$$2CH_3I + Ag_2 = Ag_2I_2 + C_2H_6;$$

and at the same temperature from zinc methyl and methylic iodide:

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

On opening the closed tubes it is evolved with great violence.

By the electrolysis of potassic acetate in concentrated aqueous solution, it is evolved, together with carbonic anhydride, at the positive pole:



$$\begin{array}{l}CH_3\\ | \\ CO\\ \ \diagdown\\ \quad OK\end{array} + \begin{array}{l}CH_3\\ | \\ CO\\ \ \diagdown\\ \quad OK\end{array} + H_2O = \begin{array}{l}CH_3\\ | \\ CH_3\end{array} + CO_2 + CO(OK)_2 + H_2.$$

It occurs pretty regularly in coal gas, and also in crude American petroleum, in which it is absorbed by the liquid hydrocarbons.

Ethane is a colourless and odourless gas of density 1·036; it has been liquefied at a pressure of 46 atmospheres at 4°. It is nearly insoluble in water, but soluble in a little less than its own volume of alcohol. By action of diffused daylight on a mixture of equal volumes of chlorine and ethane, there results, as first substitution-product, monochlor-ethane or ethylic chloride:

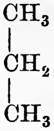
$$C_2H_6 + Cl_2 = HCl + C_2H_5Cl,$$

from which all the other ethylic compounds can be prepared. At the same time, especially when the chlorine is in excess, substitution-products richer in chlorine are formed.

Propane, C_3H_8.

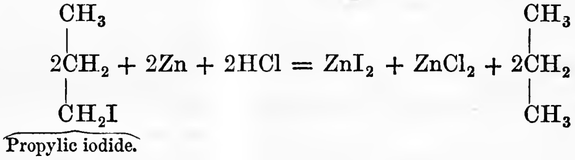
(Propylic hydride, $C_3H_7.H$, or ethyl-methyl, $\begin{array}{c}C_2H_5\\|\\CH_3\end{array}$)

Structural formula

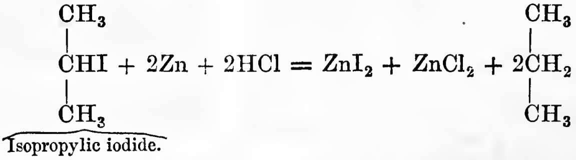


$$\begin{array}{c}CH_3\\|\\CH_2\\|\\CH_3\end{array}$$

153. Occurs in crude petroleum, and is obtained from the propyl compounds in a similar manner to ethane, most easily by action of zinc and hydrochloric acid upon both propylic iodides:

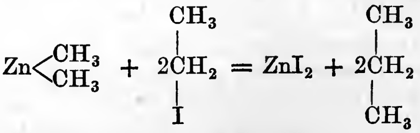


$$\underbrace{2\begin{array}{c}CH_3\\|\\CH_2\\|\\CH_2I\end{array}}_{\text{Propylic iodide.}} + 2Zn + 2HCl = ZnI_2 + ZnCl_2 + 2\begin{array}{c}CH_3\\|\\CH_2\\|\\CH_3\end{array}$$



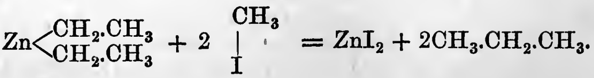
$$\underbrace{\begin{array}{c}CH_3\\|\\CHI\\|\\CH_3\end{array}}_{\text{Isopropylic iodide.}} + 2Zn + 2HCl = ZnI_2 + ZnCl_2 + 2\begin{array}{c}CH_3\\|\\CH_2\\|\\CH_3\end{array}$$

Without doubt the same body is obtained by heating a mixture of zinc methyl with ethylic iodide, or of zinc ethyl with methylic iodide:



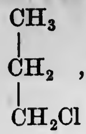
$$Zn<\begin{array}{l}CH_3\\CH_3\end{array} + 2\begin{array}{c}CH_3\\|\\CH_2\\|\\I\end{array} = ZnI_2 + 2\begin{array}{c}CH_3\\|\\CH_2\\|\\CH_3\end{array}.$$

or



$$Zn<\begin{array}{l}CH_2.CH_3\\CH_2.CH_3\end{array} + 2\begin{array}{c}CH_3\\|\\I\end{array} = ZnI_2 + 2CH_3.CH_2.CH_3.$$

Propane is a colourless gas, which liquefies below −20°, and of which six volumes are absorbed by one volume of alcohol. By action of chlorine in diffused daylight there result, as the first substitution-products, the isomeric compounds:

propylic chloride, 

$$\begin{array}{c} CH_3 \\ | \\ CH_2 \\ | \\ CH_2Cl \end{array}$$

, and isopropylic chloride, 

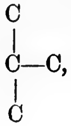
$$\begin{array}{c} CH_3 \\ | \\ CHCl \\ | \\ CH_3 \end{array}$$

Butanes or Tetranes, C_4H_{10}.

154. As four carbon atoms can combine in two different ways to form a tetra-carbon nucleus:

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

and



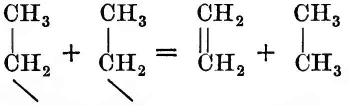
$$\begin{array}{l} C \\ | \\ C—C, \\ | \\ C \end{array}$$

two butanes can exist, and both have been prepared.

Normal butane, butylic hydride, diethyl, or propyl-methyl, occurs in crude petroleum, and is formed, as diethyl, by action of zinc or sodium upon ethylic iodide, or by the decomposition of zinc ethyl by this latter in sealed tubes heated to at least 150°:

$$Zn{<}\begin{array}{l} CH_2.CH_3 \\ CH_2.CH_3 \end{array} + \begin{array}{l} CH_3.CH_2I \\ CH_3.CH_2I \end{array} = ZnI_2 + 2CH_3.CH_2.CH_2.CH_3.$$

Ethylene and ethane are formed as secondary products during this reaction, one ethyl group, with double linking of its own carbon atoms, yielding hydrogen to the other:

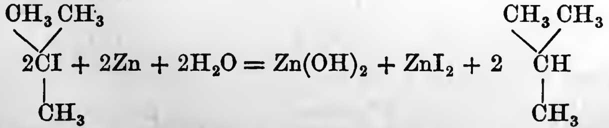


$$\begin{array}{c} CH_3 \\ | \\ CH_2 \end{array} + \begin{array}{c} CH_3 \\ | \\ CH_2 \end{array} = \begin{array}{c} CH_2 \\ \| \\ CH_2 \end{array} + \begin{array}{c} CH_3 \\ | \\ CH_3 \end{array}$$

On opening the cooled tube, which contains the butane liquefied by the pressure, a mixture of both gases is given off with great violence; later the butane evaporates, and can be condensed in a vessel cooled by a mixture of ice and salt.

Butane is, at ordinary temperatures, a colourless gas of ethereal odour, and of density 2·046; it becomes liquid at + 3° under a pressure of 2½ atmospheres; its boiling point is about + 1°. It is nearly insoluble in water, pretty readily soluble in alcohol, this latter absorbing 18 times it own volume at 14°.

Isobutane, isobutylic hydride, or trimethyl methane, isomeric with the foregoing, is obtained by action of zinc and water upon the iodide from trimethyl carbinol:

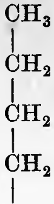


$$2\begin{array}{c} CH_3\,CH_3 \\ \diagdown\,\diagup \\ CI \\ | \\ CH_3 \end{array} + 2Zn + 2H_2O = Zn(OH)_2 + ZnI_2 + 2\begin{array}{c} CH_3\,CH_3 \\ \diagdown\,\diagup \\ CH \\ | \\ CH_3 \end{array}$$

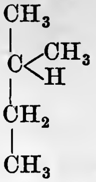
It is a colourless gas, which is condensable to a liquid at −17°.

Pentanes, C_5H_{12}.

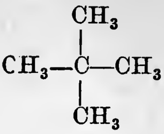
155. Corresponding to the three forms of a pentacarbon nucleus, three pentanes may exist, namely :



Normal pentane.
Normal amylic hydride.
Ethyl-propyl
or methyl-butyl.



Isopentane.
Isoamylic hydride.
Isopropyl-ethyl.
Isobutyl-methyl.



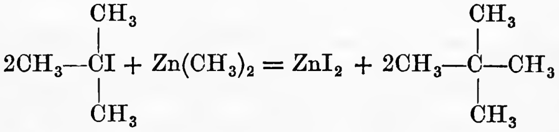
Tetramethyl methane.

Both the former exist in American petroleum, and are obtainable therefrom by fractional distillation.

Normal pentane is also found in the light tar oils, from the distillation of cannel coal; it is a mobile colourless liquid, which boils at 37°–39°.

The boiling point of the closely analogous *isopentane* is about 30°; it is prepared synthetically by the decomposition of fermentation amylic iodide with zinc and water. It mixes in every proportion with alcohol, but not with water. At − 24° it is still liquid. The density of the liquid is ·626.

Tetramethyl methane results from the action of zinc methyl on tertiary butylic iodide:



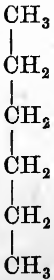
$$2CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}I + Zn(CH_3)_2 = ZnI_2 + 2CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-CH_3$$

as a colourless mobile liquid, which boils at + 9·5°, and solidifies to a crystalline mass at − 20°.

Hexanes, C_6H_{14}.

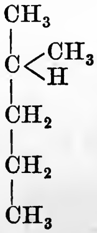
156. The hexane formula admits of five isomeric modifications :

1.



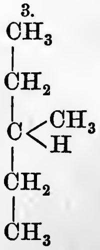
Normal hexane.
Dipropyl.
Butyl-ethyl.
Methyl-amyl.

2.



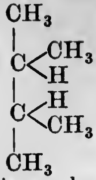
α Isohexane.
Propyl-isopropyl.
Ethyl-isobutyl.
Methyl-isoamyl.

3.



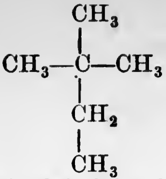
β Isohexane.
Diethyl-methyl methane.

4.



Diisopropyl,
α dimethyl butane.

5.



$$\begin{matrix} & CH_3 & \\ & | & \\ CH_3— & C & —CH_3 \\ & | & \\ & CH_2 & \\ & | & \\ & CH_3 & \end{matrix}$$

Trimethyl-ethyl methane.
Isobutyl-ethyl.

1. *Normal hexane* is obtained by action of zinc and water, or of zinc and hydrochloric acid, upon secondary normal hexylic iodide, $CH_3.CH_2.CH_2.CH_2.CHI.CH_3$ (which results from the action of hydriodic acid upon mannite), as a colourless liquid, boiling at 69°–70°, and of sp. gr. ·663 at 17°. It is also prepared by decomposition of an ethereal solution of propylic iodide by sodium :

$$2CH_3.CH_2.CH_2I + Na_2 = 2NaI + CH_3.CH_2.CH_2.CH_2.CH_2.CH_3,$$

and occurs in petroleum and light coal-tar oil.

2. α *Isohexane* is obtained, as ethyl-isobutyl, by action of sodium on an ethereal solution of a mixture of ethylic and isobutylic iodides:

$$CH_3.CH_2I + I.CH_2.CH.\left\{\begin{matrix}CH_3\\CH_3\end{matrix}\right. + Na_2 = 2NaI + CH_3.CH_2.CH_2.CH{<}\begin{matrix}CH_3\\CH_3\end{matrix};$$

it boils at 62°, and has sp. gr. ·7011 at 0°.

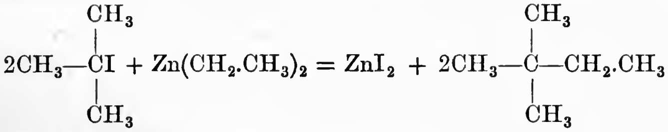
3. β *Isohexane* has not yet been prepared.

4. *Diisopropyl* is obtained by de-iodising ispropylic iodide in ethereal solution by sodium:

$$2\begin{matrix}CH_3\\CH_3\end{matrix}{>}CHI + Na_2 = 2NaI + \begin{matrix}CH_3\\CH_3\end{matrix}{>}CH—CH{<}\begin{matrix}CH_3\\CH_3\end{matrix}$$

as a colourless liquid, boiling at 58° and having sp. gr. ·6769 at 10°.

5. *Trimethyl-ethyl methane* is prepared by action of zinc ethyl upon tertiary butylic iodide :



$$\begin{matrix} & CH_3 \\ & | \\ 2CH_3— & CI \\ & | \\ & CH_3 \end{matrix} + Zn(CH_2.CH_3)_2 = ZnI_2 + \begin{matrix} & CH_3 & \\ & | & \\ 2CH_3— & C & —CH_2.CH_3 \\ & | & \\ & CH_3 & \end{matrix}$$

It boils at 43°–48°.

Higher Homologues.

157. The number of possible isomers of every member of these series increases with the increase of the number of carbon atoms in the nucleus ; but few of them, however, are known, and will now be shortly noticed.

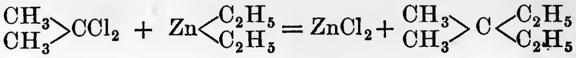
Heptanes, C_7H_{16}.—*Normal heptane,*

$$CH_3—CH_2—CH_2—CH_2—CH_2—CH_2—CH_3,$$

is contained in coal-tar oil and in petroleum ; it is a liquid boiling at 97·5.

α *Isoheptane,* $CH_3.CH_2.CH_2.CH_2.CH.{<}\begin{matrix}CH_3\\CH_3\end{matrix}$, is obtained as ethyl-isoamyl, by decomposition of a mixture of fermentation amylic iodide and ethylic iodide by sodium, as an oil boiling at 88°–90°.

Dimethyl-diethyl methane or *carb-dimethyl-diethyl*, $\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}>C<\begin{smallmatrix}CH_2.CH_3\\CH_2.CH_3\end{smallmatrix}$, results from the action of zinc ethyl upon acetonylic chloride:



$$\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}>CCl_2 + Zn<\begin{smallmatrix}C_2H_5\\C_2H_5\end{smallmatrix} = ZnCl_2 + \begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}>C<\begin{smallmatrix}C_2H_5\\C_2H_5\end{smallmatrix}$$

It boils at 86°.

Triethyl methane, $CH_3.CH_2.CH<\begin{smallmatrix}CH_2.CH_3\\CH_2.CH_3\end{smallmatrix}$ or $CH(C_2H_5)_3$, is formed amongst other products by warming ethylic orthoformate with zinc ethyl:

$$\underset{\text{Ethylic orthoformate.}}{2CH.(O.C_2H_5)_3} + \underset{\text{Zinc ethyl.}}{3Zn(C_2H_5)_2} = \underset{\text{Zinc ethylate.}}{3Zn(O.C_2H_5)_2} + 2CH.(C_2H_5)_3$$

It is a colourless, faint-smelling liquid of sp. gr. ·689 at 27°, and boiling at 96°.

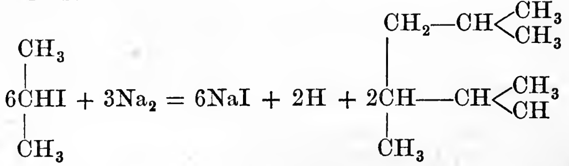
Octanes, C_8H_{18}.—*Normal octane*,

$$CH_3—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_3,$$

or dibutyl, is formed from two molecules of normal butylic iodide ($CH_3—CH_2—CH_2—CH_2I$) by de-iodising with sodium; it boils at 123°–125°, and has the sp. gr. ·7032. It is also obtained from normal octyl alcohol, and from methyl-hexyl carbinol, and occurs in mineral oil.

Diisobutyl, $\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}>CH—CH_2—CH_2—CH<\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}$, is prepared from isobutylic iodide and sodium, as a liquid boiling at 109°, and of sp. gr. ·7057.

Nonanes, C_9H_{20}.—There are two known, namely, *isobutyl-isoamyl*, $\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}>CH.CH_2.CH_2.CH_2.CH<\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}$, prepared from the iodides of the respective alcohol radicals, which boils at 132°, and a body boiling at 130°, obtained in small quantity by action of sodium amalgam upon isopropylic iodide:

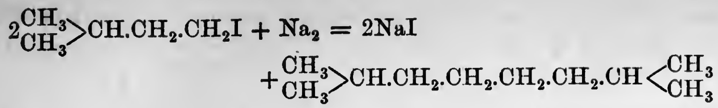


$$6\begin{matrix}CH_3\\|\\CHI\\|\\CH_3\end{matrix} + 3Na_2 = 6NaI + 2H + 2\begin{matrix}CH_2—CH<\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}\\|\\CH——CH<\begin{smallmatrix}CH_3\\CH\end{smallmatrix}\\|\\CH_3\end{matrix}$$

This may be termed *propylene diisopropyl*, the group $CH_2—CH—CH_3$ being the radical of the propylene compounds.

A third, probably *normal nonane*, occurs in petroleum, and also in the mixture of hydrocarbons obtained by the action of heat on solid paraffin; it boils at 147°–148°; sp. gr. ·7279 at 13·5.

Decanes, $C_{10}H_{22}$.—One decane has been known for a long time under the name of *diamyl*, more correctly *diisoamyl*. It is prepared from fermentation amylic iodide by action of zinc or sodium:



$$2\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH.CH_2.CH_2I + Na_2 = 2NaI + \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH.CH_2.CH_2.CH_2.CH_2.CH<\!\!\begin{matrix}CH_3\\CH_3\end{matrix}$$

It is a colourless oil of faint ethereal odour and burning taste; has sp. gr. ·77 and boils at 158°.

A hydrocarbon of the same composition results by heating oil of turpentine with much concentrated hydriodic acid to 275°:

$$C_{10}H_{16} + 6HI = C_{10}H_{22} + 3I_2.$$

It distils over between 155° and 162°.

158. A number of higher members of the series have been isolated from American petroleum and coal tar by fractional distillation; their constitution is, however, still unknown.

These compounds are:

$C_{12}H_{26}$	having	the boiling	point	198°–200°
$C_{13}H_{28}$	,,	,,	,,	218°–220°
$C_{14}H_{30}$	,,	,,	,,	236°–240°
$C_{15}H_{32}$	,,	,,	,,	258°–262°
$C_{16}H_{34}$	,,	,,	,,	about 280°

A synthetically prepared *dodecane* is obtained by the electrolysis of potassic œnanthate, ($C_6H_{13}.CO.OK$), as an oil boiling at 202°; the normal *hexdecane*, $C_{16}H_{34}$ or $CH_3—(CH_2)_{14}—CH_3$, is obtained as a bye product in the preparation of normal octane from normal octylic iodide; it boils at 278°.

159. Paraffins containing more than 16 carbon atoms are contained in those oils, &c., boiling above 300° contained in petroleum, and obtained in the dry distillation of peat, lignite, &c., but have not yet been isolated. The substance commercially termed *paraffin* consists essentially of them; this mixture, which probably also contains hydrocarbons of the formula C_nH_{2n}, forms a colourless translucent mass, which, according to its source and method of purification, melts between 40° and 80°. It is insoluble in water, little soluble in cold alcohol, more readily in hot alcohol, ether, and liquid hydrocarbons; it is one of the materials used for the manufacture of candles.

To prepare it the high-boiling portions of peat or lignite tar, partly solidified by cooling, are heated with concentrated sulphuric acid; this destroys one series of impurities and changes others into sulphur containing acids (sulphonic acids) soluble in water, whilst the fused paraffin is not itself attacked, and collects on the surface as an oily layer. This is separated from the acid aqueous solution, and submitted to distillation after addition of some caustic alkali to neutralise any adhering acid. The distillate is then mixed with not too large a quantity of colourless light tar-oil, brought to crystallisation by cooling, and the oil (which dissolves out colouring matters and oily impurities) expressed by aid of hydraulic presses. The residue is paraffin.

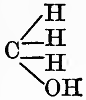
On account of its difficult alterability by most of those reagents which act powerfully on organic bodies, it obtained its name of paraffin (from *parum affinis*), which later was adopted as the general name for the whole series.

MONOSUBSTITUTION PRODUCTS OF THE PARAFFINS.

DERIVATIVES OF THE MONOVALENT ALCOHOL RADICALS OR ALKYLS, C_nH_{2n+1}.

General.

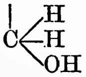
160. The monovalent alcohols, $C_nH_{2n+1}.OH$, may be arranged in three classes according to the position of the carbon atom united to hydroxyl in the nucleus, to which methyl alcohol or carbinol,



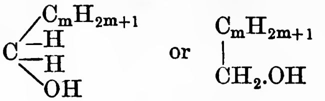
the first member of the series, may be added as a fourth variety.

1. The *primary alcohols* contain the hydroxyl group attached to a terminal primarily united carbon atom, which, therefore, is also united to two hydrogen atoms; the group

$CH_2.OH$

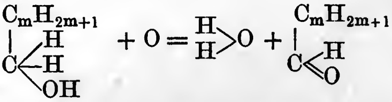


is characteristic of them. From methyl alcohol they are derived by replacement of *one* methyl hydrogen atom by an alcohol radical:

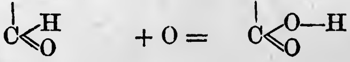


$= C_nH_{2n+1}.OH$ (if $_{m+1} = {}_{n}$).

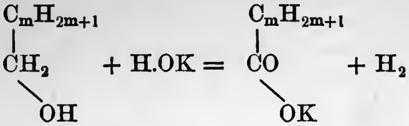
By action of oxidising agents upon them there results, according to the extent of oxidation, two products—namely, by action of one atom of oxygen with elimination of two hydrogen atoms, *aldehydes:*



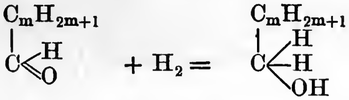
which are converted by a second atom of oxygen into monobasic acids:



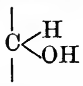
The oxidation of the primary alcohols to acids of equal carbon contents can also be effected by action of alkalies at high temperatures :



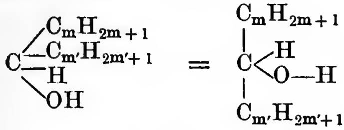
The primary alcohols can be regenerated from the aldehydes by action of nascent hydrogen :



2. *Secondary alcohols* are those in which hydroxyl is united to a secondarily combined carbon atom (that is, one which is united to *two* other carbon atoms) ; they are therefore characterised by the group



From carbinol they are derived by replacement of *two* hydrogen atoms by alcohol radicals :

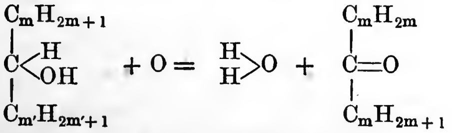


$= C_nH_{2n+1}OH$ (if $m + m' + 1 = n$).

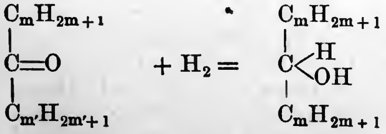
As m and m' must at least $= 1$, the lowest member of the series must contain three carbon atoms :

$$CH_3—CH(OH)—CH_3 = \text{dimethyl carbinol.}$$

Oxidising agents, as long as the carbon chain is not destroyed, act with only one oxygen atom upon the molecule of a secondary alcohol ; there results thereby, with removal of two hydrogen atoms (as in the formation of aldehydes), *ketones :*

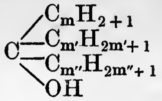


from which the secondary alcohol can be regenerated by nascent hydrogen :



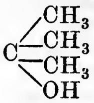
3. *Tertiary alcohols* contain their hydroxyl united to a carbon

atom, which is united to three other carbon atoms. Therefore they appear as carbinol in which *all* the non-hydroxylic hydrogen atoms are replaced by alcohol radicals :

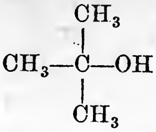


$= C_nH_{2n+1}.OH$ (if $_{m+m'+m''+1} = {}_n$).

The lowest tertiary alcohol, therefore, contains four carbon atoms :



or

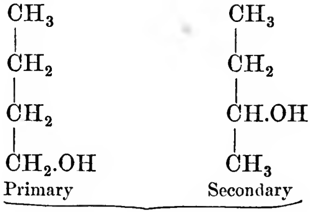


$CH_3—\overset{CH_3}{\underset{CH_3}{C}}—OH$

The tertiary alcohols are not capable of an oxidation similar to that in aldehyde or ketone formation ; by action of powerful oxidising agents the nucleus is broken up into several smaller ones.

161. It is evident that the structure of the nucleus must have considerable influence on the nature of the alcohol ; there are to be distinguished :

1. *Normal alcohols*, whose nuclei can contain only primarily and secondarily combined carbon atoms, and therefore a single chain with only two terminal carbon atoms. Normal alcohols may be primary or secondary, but not tertiary :

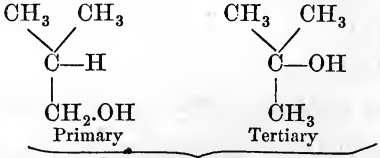


Primary Secondary

Normal butyl alcohols.

2. *Isoalcohols*, which are derived from nuclei containing side chains, and therefore tertiarily or quarternarily united, contain more than two terminal carbon atoms.

There are primary, tertiary, and also secondary isoalcohols when with more than five atoms of carbon :



Primary Tertiary

Isobutylic alcohols.

162. Although the alcohols have no action on vegetable colours, still they have the properties of weak basic hydrates, appearing therefore as the hydroxyl compounds of electro-chemically positive radicals. They also react in many ways like the hydrates of the monovalent alkali metals, though with much less energy; they unite pretty readily with acids to saline compounds in which the alcohol radical replaces the acid hydrogen. By action of haloid acids upon them the chlorides of the alcohol radicals result:

$$C_nH_{2n+1}.OH + HCl = C_nH_{2n+1}Cl + OH_2,$$

like $$KOH + HCl = KCl + OH_2;$$

and they yield with the oxyacids (in complete analogy to the oxysalts of alkali metals) the ethereal salts:

$$C_nH_{2n+1}.OH + HO.NO_2 = C_nH_{2n+1}.O.NO_2 + H_2O;$$

like $$KOH + HO.NO_2 = K.O.NO_2 + H_2O,$$

$$C_nH_{2n+1}.OH + H_2SO_4 = C_nH_{2n+1}.HSO_4 + H_2O;$$

like $$KOH + H_2SO_4 = K.HSO_4 + H_2O,$$

$$2(C_nH_{2n+1}.OH) + H_2SO_4 = (C_nH_{2n+1})_2SO_4 + 2H_2O;$$

like $$2KOH + H_2SO_4 = K_2SO_4 + 2H_2O, \text{ \&c.}$$

Formation of Alcohols.

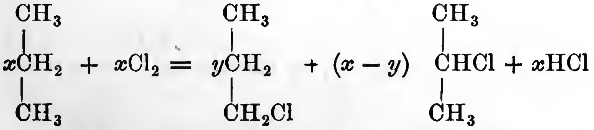
163. Many alcohols of the series $C_nH_{2n+1}.OH$ occur in nature as the salts of organic acids, and indeed ready formed in plants and animals; many of them result from the fermentation of saccharine bodies by an organised ferment—yeast—and then accompany ethyl alcohol. In their synthetical preparation from the paraffins the use of the monochlor substitution products of these latter is indispensable, the conversion of the chloride into the alcohol being usually effected in this manner: the chloride is first converted into the acetate by heating with argentic or potassic acetates:

$$C_nH_{2n+1}.Cl + KO.C_2H_3O = C_nH_{2n+1}.O.C_2H_3O + KCl.$$

and this, on heating with potassic hydrate solution, yields the alcohol and potassic acetate:

$$C_nH_{2n+1}.O.C_2H_3O + KHO = KO.C_2H_3O + C_nH_{2n+1}.OH.$$

When the paraffin contains more than two carbon atoms, the first action of chlorine produces isomeric chlorides, from the mixture of which, when heated in the above way, secondary, &c., alcohols are obtained as well as primary. For instance, propane, by treatment with chlorine, yields simultaneously primary and secondary propylic chlorides:

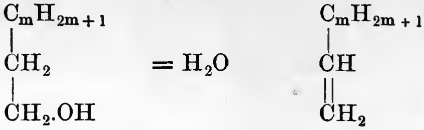


$$\begin{array}{c}CH_3\\ |\\ xCH_2\\ |\\ CH_3\end{array} + xCl_2 = \begin{array}{c}CH_3\\ |\\ yCH_2\\ |\\ CH_2Cl\end{array} + (x-y)\begin{array}{c}CH_3\\ |\\ CHCl\\ |\\ CH_3\end{array} + xHCl$$

and there are finally obtained both primary and secondary propylic alcohols.

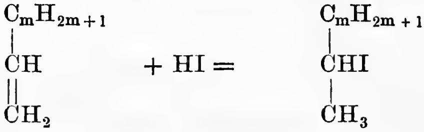
Many *primary alcohols* have only been obtained by the action of nascent hydrogen upon those aldehydes which they themselves would yield on oxidation.

Secondary alcohols are correspondingly prepared by hydrogenising ketones. Primary alcohols can be converted into those secondary alcohols which have the OH group attached to the carbon atom next to the primary position in the following manner:—The primary alcohol is converted by dehydrating agents (by heating with concentrated sulphuric acid or zincic chloride) into a hydrocarbon, C_nH_{2n} (olefine):



$$\begin{array}{l} C_mH_{2m+1} \\ | \\ CH_2 \\ | \\ CH_2.OH \end{array} \quad = H_2O \quad \begin{array}{l} C_mH_{2m+1} \\ | \\ CH \\ \| \\ CH_2 \end{array}$$

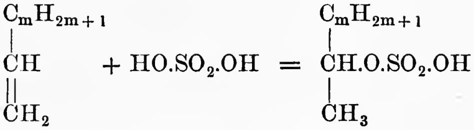
and the latter then gently heated with concentrated hydriodic acid. One molecule of this is taken up, the iodine going into the secondary, the hydrogen into the primary, position:



$$\begin{array}{l} C_mH_{2m+1} \\ | \\ CH \\ \| \\ CH_2 \end{array} \quad + HI = \quad \begin{array}{l} C_mH_{2m+1} \\ | \\ CHI \\ | \\ CH_3 \end{array}$$

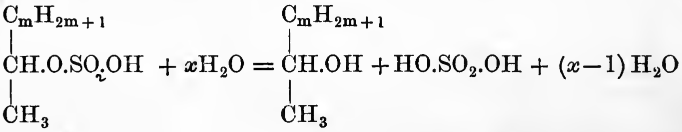
The secondary alcoholic iodide is then converted into acetate by heating with potassic acetate, and finally into the secondary alcohol by treatment with potassic hydrate.

This transformation can be still more simply effected by absorbing the olefine in concentrated sulphuric acid. By the same law of the easier combination of negative elements or radicals to an intermediate than to a terminal carbon atom, the acid sulphate formed is that of the secondary alcohol:



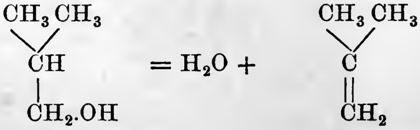
$$\begin{array}{l} C_mH_{2m+1} \\ | \\ CH \\ \| \\ CH_2 \end{array} \quad + HO.SO_2.OH \quad = \quad \begin{array}{l} C_mH_{2m+1} \\ | \\ CH.O.SO_2.OH \\ | \\ CH_3 \end{array}$$

which by treatment with an alkali, or by boiling with a large excess of water, yields the secondary alcohol:

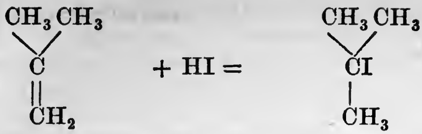


$$\begin{array}{l} C_mH_{2m+1} \\ | \\ CH.O.SO_2.OH \\ | \\ CH_3 \end{array} + xH_2O = \begin{array}{l} C_mH_{2m+1} \\ | \\ CH.OH \\ | \\ CH_3 \end{array} + HO.SO_2.OH + (x-1)\,H_2O$$

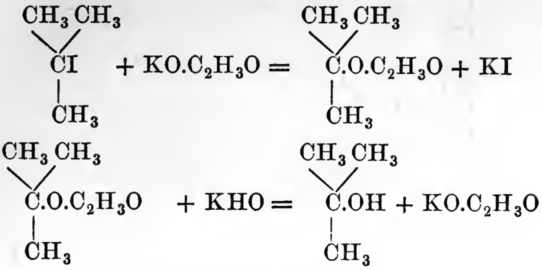
Tertiary alcohols can be similarly prepared from primary alcohols in which the $CH_2.OH$ group is directly united with a tertiarily combined carbon atom:



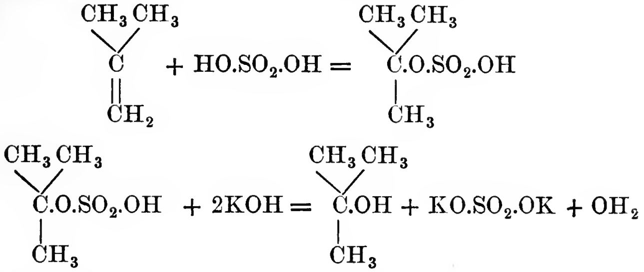
Primary isobutylic alcohol. Isobutylene.



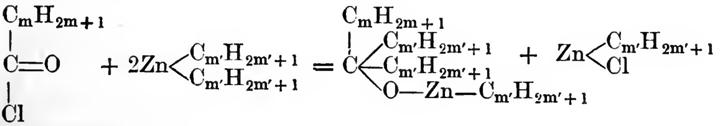
(Tertiary butylic iodide or trimethyl carbiniodide.)



Just the same result is arrived at by the use of sulphuric acid:

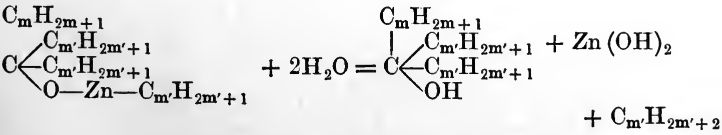


A general method of preparing tertiary alcohols is by the action of the chlorides of monobasic acid radicals on the zinc compounds of the alcohol radicals:



Acid chloride.

When the product of this reaction is heated with water, a paraffin, zincic hydrate, and a tertiary alcohol result:

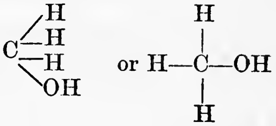


The Alcohols.

164. The homologous series $C_nH_{2n+2}O$ or $C_nH_{2n+1}.OH$ includes members of from one to thirty carbon atoms, together with their isomers. In many cases members are still missing. The known members are :

CH_4O	or	$CH_3.OH$	methylic alcohol.
C_2H_6O	,,	$C_2H_5.OH$	ethylic alcohol.
C_3H_8O	,,	$C_3H_7.OH$	propylic alcohol.
$C_4H_{10}O$	,,	$C_4H_9.OH$	butylic alcohols.
$C_5H_{12}O$	,,	$C_5H_{11}.OH$	amylic alcohols.
$C_6H_{14}O$	,,	$C_6H_{13}.OH$	hexylic alcohols.
$C_7H_{16}O$	,,	$C_7H_{15}.OH$	heptylic alcohols.
$C_8H_{18}O$	,,	$C_8H_{17}.OH$	octylic alcohols.
$C_9H_{20}O$	,,	$C_9H_{19}.OH$	nonylic alcohols.
$C_{10}H_{22}O$	,,	$C_{10}H_{21}.OH$	decylic alcohols.
—		—	
—		—	
—		—	
—		—	
$C_{16}H_{34}O$	,,	$C_{16}H_{33}.OH$	cetylic alcohol.
—		—	
—		—	
—		—	
$C_{27}H_{56}O$	,,	$C_{27}H_{55}.OH$	cerylic alcohol.
—		—	
—		—	
—		—	
$C_{30}H_{62}O$	,,	$C_{30}H_{61}.OH$	mellissylic alcohol

Carbinol, or Methylic Alcohol, $CH_3.OH =$



$$C\begin{cases}H\\H\\H\\OH\end{cases} \quad \text{or} \quad H-\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-OH$$

165. Carbinol, commonly called wood spirit, results from the dry distillation of wood; the aqueous layer of the distillate contains in addition several other bodies, such as acetic acid, acetone, &c. As the boiling point of carbinol is considerably lower than that of water, on distilling the wood-tar water—previously mixed with lime to fix the acetic acid—all the methylic alcohol is contained in the first tenth of the distillate. This first fraction still contains, however, acetone and water; to remove the latter it is rectified over quick-lime; the distillate containing the wood spirit and acetone is added to fused calcic chloride, which combines with the first, so that the unchanged acetone, which is readily volatile, may be driven off by heating in a water bath. The residue, the compound of carbinol and calcic chloride, is now mixed with water, whereby, with formation of $CaCl_2,6H_2O$, the carbinol is set free, and on distillation passes over, together with a little water. By repeated rectification over quick-lime it is obtained anhydrous. In the preparation so obtained there are still some impurities adhering obstinately to it, which communicate a burning taste. It is obtained quite pure by conversion into its oxalate, which, being crystallisable, is easily purified, and then retransformed into the alcohol by potassic hydrate.

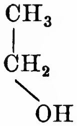
Carbinol can also be prepared from the ethereal oil of *gaultheria procumbens* (the North American winter-green shrub). This contains methylic salicylate, mixed with hydrocarbons; the first, on boiling with an alkali, yields a salicylate and methylic alcohol.

Carbinol is a colourless, mobile, spirituous-smelling liquid, of sp. gr. ·814 at 4°; it boils at 60°, is readily inflammable, and burns with a slightly luminous flame. It mixes in every proportion with water, ethylic alcohol, and ether, in the first case with diminution of volume and evolution of heat. By oxidising agents, e.g. air in contact with platinum black, it is converted into formic aldehyde and formic acid. By passing its vapour over heated soda lime a formate is produced:

$$CH_3.OH + NaOH = CHO.ONa + 2H_2.$$

It is a good solvent for many substances insoluble in water, such as fats or ethereal oils, and for many salts; e.g. calcic chloride, especially on heating, is dissolved by it in considerable quantity; the saturated liquid, on cooling, gives leafy crystals of a compound, in which methylic alcohol is united to calcic chloride like water of crystallisation. This compound is not decomposed at 100°.

Methyl Carbinol, or Ethylic Alcohol, $C_2H_5.OH =$



$$C_2H_5.OH = \begin{array}{l} CH_3 \\ \,| \\ CH_2 \\ \quad\searrow \\ \qquad OH \end{array}$$

166. Ethylic alcohol, or *spirits of wine*, more commonly known as alcohol only, results from the fermentation of many saccharine bodies, whereby these nearly entirely decompose into carbonic anhydride and alcohol:

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

There are also some other products formed, such as succinic acid, glycerine, and higher members of the alcohol series, which latter are known as fusel oils or fusel alcohols.

The ferment essential to the alcoholic fermentation is yeast, a one-celled organism, propagating by budding, which, under favourable conditions, causes the decomposition of the sugar to occur with great quickness, and with evolution of heat, when placed in contact with its solutions. To the conditions necessary belong the temperature, which must not be below 0° nor above 35°; the presence both of certain mineral substances (especially phosphates) and of nitrogenous organic matters, which serve as food for the yeast; and, finally, sufficient dilution of the sugar solution. If this latter be too concentrated it is either not at all transformed, or the fermentation ceases in consequence of the death of the yeast cells. A liquid containing more than 20–22 % of sugar cannot be completely fermented by yeast. Many poisonous substances, e.g. phenol, even in small quantity in an otherwise favourably mixed solution, prevent fermentation by killing the yeast cells.

Alcohol, which boils at a lower temperature than water, can be obtained more pure from the fermented liquid by fractional distillation. It is then found in the first fractions, whilst water and the non-volatile matters—namely, the yeast and the marc—remain behind, the latter retaining the chief portion of the fusel oils. By repeated fractional distillation the spirit is obtained more and more concentrated, and separated from the still lower boiling admixtures ('first runnings'). The strongest rectified spirit still contains 5–10 % of water and some fusel oils. The first can be removed by chemical means, the latter by means of filtration through porous carbon.

As dehydrating agents, all energetically hygroscopic substances may be employed, especially such as do not combine with alcohol—e.g. ignited potassic carbonate, quick-lime, &c. Usually the strongest spirit is placed on quick-lime for 24 hours, with frequent shaking, then distilled from a water bath, and the distillate heated anew in similar manner. The last traces of water are removed by treatment with sodium, followed by distillation.

The smallest traces of water in alcohol may be detected by bringing it in contact with cupric sulphate, dried till colourless, when a blue colouration indicates the presence of water.

167. *Absolute*, i.e. entirely anhydrous and pure, ethylic alcohol is a colourless, mobile liquid of agreeable odour and burning taste, of sp. gr. ·8063 at + 4° and ·7895 at 20°. It boils under normal atmospheric pressure at 78·5°, and is still liquid at − 90°. Easily inflamed, it burns with a bluish, feebly luminous flame. It is a strong poison.

Absolute alcohol possesses a very considerable affinity for water; it therefore dries damp substances energetically, and acts as an antiseptic. On mixing water with alcohol, heat is evolved, and contraction, i.e. diminution of volume, takes place. This is most considerable when 52·3 volumes of alcohol are added to 47·7 volumes of water, the volume of the mixture being only 96·4. It appears as if a compound was formed of both in molecular quantities, as these proportions are sufficiently near to be represented by the formula $C_2H_6O,3H_2O$. Alcohol more dilute than this does not apparently act as a drying agent.

In consequence of this diminution of volume, the alteration of the sp. gr. is not proportional to that of the mixture, though additions of water increase the density. By careful investigations, the sp. gr. of a large number of synthetically prepared mixtures of alcohol and water has been determined, and by means of tables so constructed the amount of alcohol in any aqueous solution may be ascertained by determining the density.

This can be done at once in liquids containing no foreign matters, but in cases where non-volatile matters are present, as in most alcoholic drinks, this method can no longer be directly applied, and the following is substituted:—A given volume of the solution to be tested is submitted to distillation, the first distillates, which contain all the alcohol, made up to the original volume with water, and the gravity then determined. The gravity is most quickly determined by a hydrometer, whose scale, instead of sp. gr., gives the corresponding amount of alcohol, either in % by volume (Tralle's alcoholometer) or in % by weight (Richter's alcoholometer).

The general relations between the mixed contents, by volume or by weight, and the sp. gr. is sufficiently shown by the following table:

% by Weight.	Sp. Gr. at 20°.	% by Volume.
100	·7895	100·0
90	·8180	93·2
80	·8437	85·5
70	·8678	76·9
60	·8913	67·7
50	·9140	57·8
40	·9351	46·2
30	·9540	36·1
20	·9688	24·5
10	·9820	12·3
0	·99831	0·0

water at + 4° being taken as unity.

Many substances are soluble in alcohol; these are partly soluble in water also, as calcic chloride, strontic chloride, lithic chloride, many nitrates, &c., whilst other bodies readily soluble in water, such as potassic chloride, sodic chloride, the sulphates and carbonates of the alkali metals, &c., are either insoluble or difficultly soluble in absolute alcohol. On the other hand, alcohol is a good solvent for many bodies difficultly soluble or quite insoluble in water, such as iodine, fatty acids, fats, alkaloids, resins, colouring matters, &c.

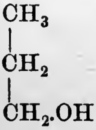
Sulphur and phosphorus are slightly soluble in it. It absorbs many gases much more than water does; 100 volumes of alcohol dissolve at 0°, 7 volumes hydrogen, 28 volumes oxygen, 13 volumes nitrogen, 52 volumes methane, 353 volumes ethylene, 433 volumes carbonic anhydride, &c.

Like methylic alcohol, it unites with many anhydrous mineral salts after the manner of water of crystallisation, e.g. with calcic chloride and with magnesic nitrate.

In commerce nothing but aqueous alcohol occurs, even that sold as absolute still containing 3–5 % of water; spirits of wine contains an amount of alcohol varying between 80 and 90 %. Still more dilute alcohol forms—mostly with small admixtures of other volatile peculiarly smelling bodies—the different 'spirits,' of which rum (from fermented sugar molasses), arrack (from rice), and cognac (distilled from wine) contain about 45–50 % by volume, the true brandies only about $\frac{1}{4}$–$\frac{1}{3}$ of their volume of alcohol. Still poorer in alcohol are those alcoholic drinks not concentrated by distillation, but prepared directly by fermentation of liquids containing sugar, such as wine (with 6–15 % of alcohol) and beer (in mean about 4–5 % of alcohol). When drunk in aqueous solution, alcohol acts as an excitant, in larger quantities as an intoxicant. It passes from the stomach and intestines into the blood, and is there in great part oxidised, but also passes in small quantity through the kidneys into the urine.

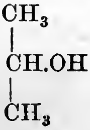
Propylic Alcohols, C_3H_8O or $C_3H_7.OH$.

168. Both the theoretically possible propylic alcohols:

1. 

$$\begin{array}{l} CH_3 \\ | \\ CH_2 \\ | \\ CH_2.OH \end{array}$$

and

2. 

$$\begin{array}{l} CH_3 \\ | \\ CH.OH \\ | \\ CH_3 \end{array}$$

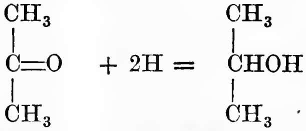
are known.

1. *Ethyl carbinol,* or *primary propylic alcohol,* occurs, mixed with ethylic alcohol and higher homologues, in many fusel oils, and it can be obtained directly therefrom with difficulty in the pure state, by very carefully conducted and repeated fractional distillations. It is more convenient to convert that portion of the fusel oils which distils between 85° and 105° into bromides (by action of phosphorous bromide), from these to isolate propylic bromide, boiling at 71°, and then to convert this latter into the acetate (§ 163), which, by boiling with an alkali, again yields the alcohol.

Ethyl carbinol is prepared synthetically by acting upon propionic aldehyde with nascent hydrogen, upon propionic anhydride with sodium amalgam, and by heating allylic alcohol with potassic hydrate.

It is a colourless, agreeable-smelling liquid, boiling at 97° and of sp. gr. ·812. It is miscible in every proportion with water, but is separated again from this solution by addition of readily soluble salts, such as calcic chloride. By oxidation it is converted into propionic aldehyde and propionic acid.

2. *Dimethyl carbinol, secondary propylic alcohol,* or *isopropylic alcohol,* is usually prepared by action of sodium amalgam upon aqueous acetone :



$$\begin{array}{c}CH_3\\|\\C{=}O\\|\\CH_3\end{array} + 2H = \begin{array}{c}CH_3\\|\\CHOH\\|\\CH_3\end{array}$$

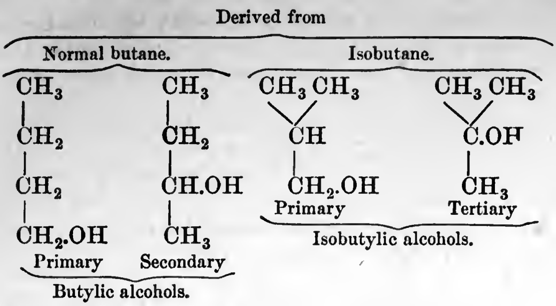
For this purpose a mixture of one part acetone and five parts water is heated with sodium amalgam until a light layer separates upon the surface of the strongly alkaline liquid. The liquid is decanted from the mercury and distilled as long as anything inflammable passes over; the distillate is then, after addition of water, again heated with sodium amalgam, &c., and this treatment continued until addition of the amalgam causes strong evolution of hydrogen. The distillate is then rectified over ignited potassic carbonate, in order to render it anhydrous, and the portion distilling below 100° rubbed together with anhydrous calcic chloride. A compound of this latter with isopropylic alcohol is formed, which is mixed with acetone. Under the receiver of an air pump the acetone evaporates, leaving the compound of calcic chloride and dimethyl carbinol as a dry powder. By heating in a retort this decomposes into its components and the alcohol distils over.

Of other methods of preparing dimethyl carbinol there may be mentioned its formation from the iodide obtained from glycerine and from propylene (see later).

Dimethyl carbinol is a colourless liquid of sp. gr. ·791 at 15°, boiling at 84°–85°; it is miscible in all proportions with pure water, ethyl alcohol, &c. By oxidising agents it is converted into acetone.

Butylic Alcohols, $C_4H_{10}O$ or $C_4H_9.OH$.

169. Theoretically there are four possible isomers of this formula —namely, two primary, one secondary, and one tertiary. They are all known :



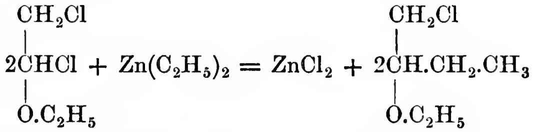
Boiling point	116°–117°	96°–98°	106°–107°	82·5°–83°
Melting ,,	liquid	liquid	liquid	25°–25·5°
Sp. gr. .	·824 at 0°	·85 at 0°	·805	·7788 at 20°

1. *Propyl carbinol*, or *normal primary butylic alcohol*, is obtained by action of nascent hydrogen upon normal butyric aldehyde. It results also from the action of sodium amalgam upon a mixture of normal butyric acid and its chloride, as butylic butyrate, which yields the alcohol on boiling with an alkali.

Propyl carbinol is a colourless, agreeable-smelling liquid, miscible in every proportion with alcohol, but not with water. On oxidation it yields normal butyric aldehyde or acid.

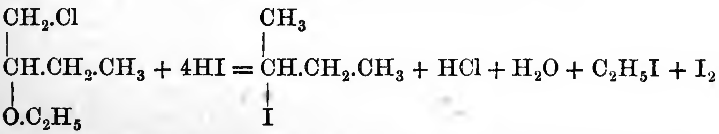
2. *Ethyl-methyl carbinol*, *normal secondary butylic alcohol*, or butylene hydrate, is most readily prepared from its iodide by converting into the acetate and saponifying the latter. Secondary butylic iodide was first prepared by action of concentrated hydriodic acid upon erythrite.

It is also obtained from the so-called bichlorether (§ 207), when this is heated with zinc ethyl :



$$2\begin{array}{l}\mathrm{CH_2Cl}\\ |\\ \mathrm{CHCl}\\ |\\ \mathrm{O.C_2H_5}\end{array} + \mathrm{Zn(C_2H_5)_2} = \mathrm{ZnCl_2} + 2\begin{array}{l}\mathrm{CH_2Cl}\\ |\\ \mathrm{CH.CH_2.CH_3}\\ |\\ \mathrm{O.C_2H_5}\end{array}$$

the resulting ethyl chlorether heated with hydriodic acid :



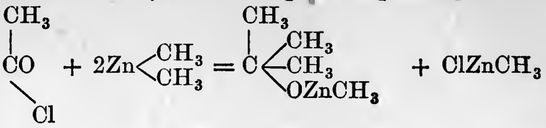
$$\begin{array}{l}\mathrm{CH_2.Cl}\\ |\\ \mathrm{CH.CH_2.CH_3}\\ |\\ \mathrm{O.C_2H_5}\end{array} + 4\mathrm{HI} = \begin{array}{l}\mathrm{CH_3}\\ |\\ \mathrm{CH.CH_2.CH_3}\\ |\\ \mathrm{I}\end{array} + \mathrm{HCl} + \mathrm{H_2O} + \mathrm{C_2H_5I} + \mathrm{I_2}$$

and the secondary butylic iodide converted into the alcohol as usual.

3. *Isopropyl carbinol*, *primary isobutylic alcohol*, or *fermentation butylic alcohol*, is obtained from most fusel oils by fractional distillation. It is liquid, smells like fusel oil, and dissolves in about ten times its weight of pure water, but is readily separated from the solution on addition of soluble salts. By oxidising agents it is converted into isobutyric aldehyde or acid.

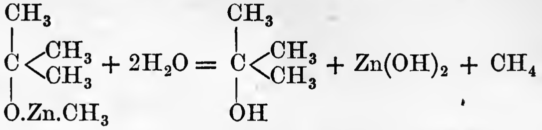
4. *Trimethyl carbinol*, or *tertiary butylic alcohol*, is contained in small quantity in many fusel oils, but is extremely difficult to separate

therefrom. It is generally prepared by allowing a mixture of one volume of chloracetyl and four volumes of zinc methyl to remain for a long time at 0°, a crystalline compound separating out :



$$\begin{array}{l}CH_3\\ |\\ CO\\ \;\diagdown\\ \;\;Cl\end{array} + 2Zn\left\langle\begin{array}{l}CH_3\\ CH_3\end{array}\right. = \begin{array}{l}CH_3\\ |\\ C\left\langle\begin{array}{l}CH_3\\ CH_3\\ OZnCH_3\end{array}\right.\end{array} + ClZnCH_3$$

which on treatment with water yields trimethyl carbinol :



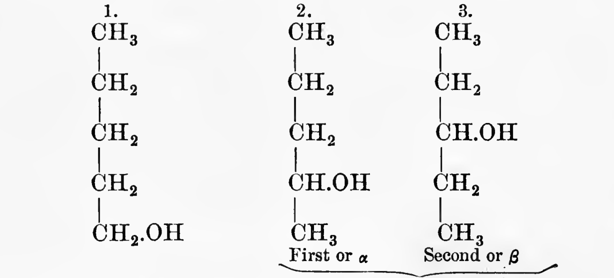
$$\begin{array}{l}CH_3\\ |\\ C\left\langle\begin{array}{l}CH_3\\ CH_3\end{array}\right.\\ |\\ O.Zn.CH_3\end{array} + 2H_2O = \begin{array}{l}CH_3\\ |\\ C\left\langle\begin{array}{l}CH_3\\ CH_3\end{array}\right.\\ |\\ OH\end{array} + Zn(OH)_2 + CH_4$$

It is prepared most conveniently from isobutylic alcohol, by converting into isobutylene, uniting the latter with sulphuric acid, and decomposing the acid sulphate with water or alkali. The complete separation of the last trace of water from trimethyl carbinol is rather difficult, as they form with one another a compound $2C_4H_{10}O,H_2O$, which boils unchanged at 80°, solidifies in a mixture of ice and salt, and has sp. gr. ·8276 at 0°. On oxidation trimethyl carbinol is mainly converted into carbonic, acetic, and propionic acids.

Pentylic or Amylic Alcohols, $C_5H_{12}O$ or $C_5H_{11}.OH$.

170. Bodies of this formula are derived from the three pentanes as follows :

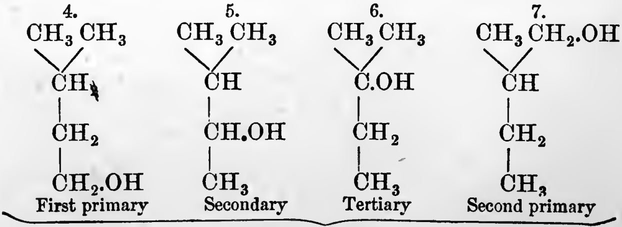
Normal pentane can yield one primary and two secondary alcohols :



$$\begin{array}{ccc}1. & 2. & 3.\\ CH_3 & CH_3 & CH_3\\ | & | & |\\ CH_2 & CH_2 & CH_2\\ | & | & |\\ CH_2 & CH_2 & CH.OH\\ | & | & |\\ CH_2 & CH.OH & CH_2\\ | & | & |\\ CH_2.OH & CH_3 & CH_3\end{array}$$

Normal amylic alcohols.

From isopentane two primary, one secondary, and one tertiary alcohol are derivable :

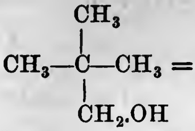


$$\begin{array}{cccc}4. & 5. & 6. & 7.\\ CH_3\;CH_3 & CH_3\;CH_3 & CH_3\;CH_3 & CH_3\;CH_2.OH\\ \diagdown\diagup & \diagdown\diagup & \diagdown\diagup & \diagdown\diagup\\ CH & CH & C.OH & CH\\ | & | & | & |\\ CH_2 & CH.OH & CH_2 & CH_2\\ | & | & | & |\\ CH_2.OH & CH_3 & CH_3 & CH_3\end{array}$$

Isoamylic alcohols.

and from tetramethyl methane only a single primary alcohol:

8.

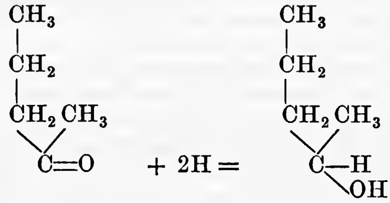


$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_2.OH}{|}}{C}}-CH_3$$ = trimethyl-carbin carbinol.

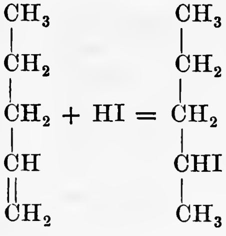
Of these numbers 1, 2, 3, 4, 5, 6 are known with certainty.

1. *Normal butyl carbinol*, or *normal primary amylic alcohol*, has only been prepared by addition of hydrogen to normal valeric aldehyde, and from normal pentane, as a colourless liquid, of fusel odour, boiling at 137°. It is insoluble in water, has sp. gr. ·8296 at 0°, and is converted into normal valeric acid on oxidation.

2. *Methyl-propyl carbinol*, or *first secondary amylic alcohol*, is prepared from propyl-methyl ketone by addition of hydrogen:



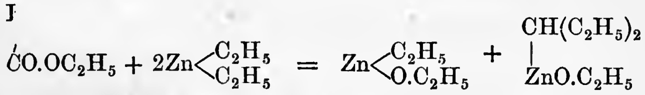
and, together with the preceding, from the chlor substitution products of normal pentane, and from ethyl-allyl by union with hydriodic acid



$$\begin{matrix} CH_3 \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CH \\ \| \\ CH_2 \end{matrix} + HI = \begin{matrix} CH_3 \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CHI \\ | \\ CH_3 \end{matrix}$$

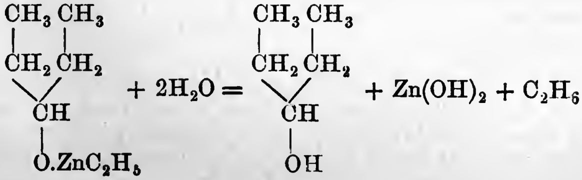
and subsequent replacement of the I by OH. It is a colourless liquid, boils at 120°–122°, and has sp. gr. ·825. By oxidation it is converted into propyl-methyl ketone.

3. *Diethyl carbinol*, or *β secondary amylic alcohol*, is prepared by heating ethylic formate with zinc ethyl:



$$\overset{H}{|}\!\!CO.OC_2H_5 + 2Zn\begin{matrix}<C_2H_5 \\ <C_2H_5\end{matrix} = Zn\begin{matrix}<C_2H_5 \\ <O.C_2H_5\end{matrix} + \begin{matrix} CH(C_2H_5)_2 \\ | \\ ZnO.C_2H_5 \end{matrix}$$

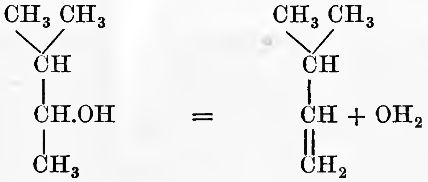
and decomposing the product with water:



It is a colourless liquid of characteristic fusel-like odour; sp. gr. ·832 at 0° and ·819 at 16°, and boils at 116°–117°; on oxidation it yields a ketone or propionic and acetic acids.

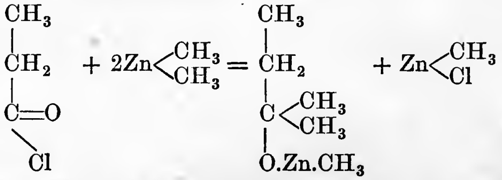
4. *Isobutyl carbinol*, or *first primary isoamylic alcohol*, is the longest known *fermentation amylic alcohol.* It occurs invariably in fusel oils, especially in that from potato spirit, and is separated from them by fractional distillation as an unpleasant, fusel-like-smelling liquid of sp. gr. ·825 at 0°, boiling at 129°–130°. It is scarcely soluble in water, but mixes in every proportion with alcohol and ether. Its vapour, when inhaled, causes coughing and acts as a poison. When quickly fractioned from fusel oil it rotates the plane of polarisation to the left slightly, but loses its optical activity on heating for a long time, or quickly if distilled from caustic alkali, without apparently undergoing any chemical change. The property of optical activity, indeed, appears to belong not to the usual isoamylic alcohol, but to a small quantity of an isomer (7 ?) mixed with it. By oxidising agents isoamylic alcohol is converted into isovaleric aldehyde and acid.

5. *Methyl-isopropyl carbinol, secondary isoamylic alcohol,* also termed *amylene hydrate,* is obtained from the isoamylene, prepared by heating 4 with zincic chloride, by uniting it with hydriodic acid, and then converting the secondary isoamylic iodide so obtained into the alcohol by means of moist argentic oxide. It boils at 106°–108°, and its vapour, on heating to 200°, splits up into isoamylene and water:



It suffers the same decomposition when mixed with sulphuric acid, without the aid of heat. On oxidation it is probably first oxidised to isopropyl-methyl ketone, but that is very readily further oxidised to carbonic and acetic acids.

6. *Ethyl-dimethyl carbinol,* or *tertiary amylic alcohol,* is obtained by the action of zinc methyl on propionic chloride:



and decomposition of the product by water. It boils at about 100°, appears not to solidify at −10°, and on oxidation yields carbonic and acetic acids.

7. *Second primary isoamylic alcohol* is probably the active admixture in fermentation amylic alcohol (4), which, though of nearly the same boiling point (125°–129°), still shows some difference from the 'active,' especially in the properties of the respective acid sulphates.

8. *Trimethyl-carbin carbinol* is not known at present.

Hexylic Alcohols, $C_6H_{14}O$ or $C_6H_{13}.OH$.

171. Of the (16) possible hexylic alcohols only some are known of still in part doubtful constitution.

1. *Amyl carbinol*, or *normal primary hexylic alcohol:*

$$CH_3.CH_2.CH_2.CH_2.CH_2.CH_2.OH,$$

is prepared mixed with butyl-methyl carbinol :

$$CH_3.CH_2.CH_2.CH_2.CH(OH).CH_3,$$

by treatment of the mixed first chlor-substitution products of normal hexane with potassic acetate, and saponification of the resulting acetates. The mixture of alcohols so formed, boiling at 149°–152°, yields on oxidation caproic acid, $CH_3.CH_2.CH_2.CH_2.CH_2.CO.OH$, and methyl-butyl ketone, $CH_3.CH_2.CH_2.CH_2.CO.CH_3$.

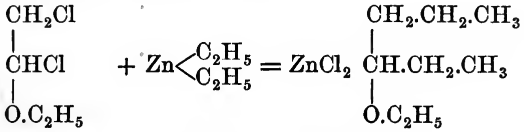
In the pure state it is obtained from the ethereal oil of *Heracleum giganteum*, which consists of hexylic butyrate and octylic acetate; by treatment with alcoholic potassic hydrate the alcohols are liberated, and are then separated by fractional distillation; it boils at 157°–158°, has sp. gr. ·819 at 23°, and gives normal caproic acid on oxidation.

2. *Methyl-butyl carbinol*, or *first normal secondary hexylic alcohol*, $CH_3.CH_2.CH_2.CH_2.CH(OH).CH_3$, is prepared from its iodide (obtained by distilling mannite with hydriodic acid) :

$$CH_3.CH_2.CH_2.CH_2.CHI.CH_3,$$

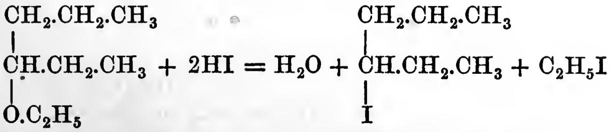
by decomposition with moist argentic oxide, as a colourless liquid insoluble in water, boiling at 137° and of sp. gr. ·8327 at 0°. On oxidation it gives, as already mentioned, methyl-butyl ketone.

3. *Ethyl-propyl carbinol*, or *second normal secondary hexylic alcohol*, $CH_3.CH_2.CH_2.CH(OH).CH_2.CH_3$, results from the decomposition of bichlor ether with zinc ethyl :



$$\begin{array}{l}CH_2Cl\\ |\\ CHCl\\ |\\ O.C_2H_5\end{array} + Zn{<}\begin{array}{l}C_2H_5\\ C_2H_5\end{array} = ZnCl_2\ \begin{array}{l}CH_2.CH_2.CH_3\\ |\\ CH.CH_2.CH_3\\ |\\ O.C_2H_5\end{array}$$

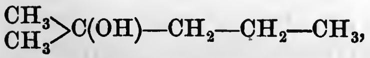
conversion into its iodide by hydriodic acid :



$$\begin{array}{l}CH_2.CH_2.CH_3\\ |\\ CH.CH_2.CH_3\\ |\\ O.C_2H_5\end{array} + 2HI = H_2O + \begin{array}{l}CH_2.CH_2.CH_3\\ |\\ CH.CH_2.CH_3\\ |\\ I\end{array} + C_2H_5I$$

and decomposition of this latter by moist argentic oxide.

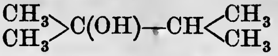
4. *Dimethyl-propyl carbinol :*



$$\begin{array}{l}CH_3\\ CH_3\end{array}{>}C(OH)—CH_2—CH_2—CH_3,$$

is prepared from butyric chloride and zinc methyl; it boils at 115° and yields acetic and propionic acid on oxidation.

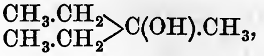
5. *Dimethyl-isopropyl carbinol:*



$$\genfrac{}{}{0pt}{}{\mathrm{CH_3}}{\mathrm{CH_3}}\!>\mathrm{C(OH)-CH}<\!\genfrac{}{}{0pt}{}{\mathrm{CH_3}}{\mathrm{CH_3}}$$

results from the action of isobutyric chloride $\left(\mathrm{Cl.CO.CH}<\!\genfrac{}{}{0pt}{}{\mathrm{CH_3}}{\mathrm{CH_3}}\right)$ on zincmethyl. It boils at 112°–115°, and solidifies at —40° to a crystalline mass.

6. *Diethyl-methyl carbinol:*



$$\genfrac{}{}{0pt}{}{\mathrm{CH_3.CH_2}}{\mathrm{CH_3.CH_2}}\!>\mathrm{C(OH).CH_3},$$

is prepared in similar manner from acetic chloride and zinc ethyl. It boils at 120°, and is completely converted into acetic acid by oxidation.

7. *Fermentation hexylic alcohol,* or *caproylic alcohol,* is separated from the fusel oil of the marc of grapes by fractional distillation. It is a light unpleasant-smelling oil, boiling at 148°–150°, and yielding caproic acid on oxidation. Its constitution has not yet been determined.

8. *Methyl-trimethyl-carbin carbinol,* $\mathrm{CH_3.CH.(OH).C}\!\begin{matrix}\diagup\mathrm{CH_3}\\ -\mathrm{CH_3}\\ \diagdown\mathrm{CH_3}\end{matrix}$, is prepared by action of nascent hydrogen on pinacoline. It boils at 120°, has sp. gr. ·834, and at low temperatures solidifies to crystals, melting at 14°; on oxidation it first yields the ketone $\mathrm{CH_3.CO.C(CH_3)_3}$, and finally carbonic and trimethacetic acid.

Heptylic Alcohols, $C_7H_{16}O$ or $C_7H_{15}.OH$.

172. A primary heptylic alcohol of unknown constitution, œnanthylic alcohol, is contained in the fusel oil of wine. It boils at 165°, and on oxidation gives œnanthic acid, $C_7H_{14}O_2$. By the distillation of castor oil with a fixed alkali a primary œnanthylic alcohol is formed, which appears to be the normal

$$\mathrm{CH_3.CH_2.CH_2.CH_2.CH_2.CH_2.CH_2.OH},$$

as it yields the same œnanthic acid on oxidation as the normal primary alcohol from normal heptane. This latter alcohol boils at 170°–172°. At the same time that its chloride is formed from normal heptane, a secondary chloride is also formed, from which *a normal secondary heptylic alcohol* or *methyl-amyl carbinol:*

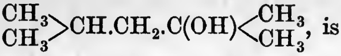
$$\mathrm{CH_3.CH_2.CH_2.CH_2.CH_2.CH(OH).CH_3},$$

is obtained as a liquid boiling at 160°–162°.

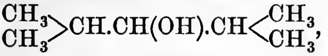
Dipropyl carbinol, $\mathrm{CH_3.CH_2.CH_2.CH(OH).CH_2.CH_2.CH_3}$, is obtained by the action of nascent hydrogen on dipropyl ketone. It boils at 149° and has sp. gr. ·814 at 25°.

Isohexyl carbinol, $\genfrac{}{}{0pt}{}{\mathrm{CH_3}}{\mathrm{CH_3}}\!>\mathrm{CH.CH_2.CH_2.CH_2.CH_2.OH}$, is obtained, together with the next-mentioned body, from the products of the chlorination of ethyl isoamyl, which are converted into acetates and then saponified. It boils at 163°–165°, and yields isoœnanthic acid on oxidation.

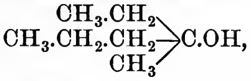
Isoamyl-methyl carbinol, $\begin{array}{l}CH_3\\CH_3\end{array}\!\!>CH.CH_2.CH_2.CH(OH).CH_3$, is prepared by the reduction of methyl-isoamyl ketone by sodium amalgam. It boils at 148°–150°, possesses a fusel-like odour, and has sp. gr. ·8185 at 17°.



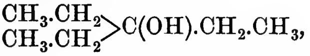
Isobutyl-dimethyl carbinol, $\begin{array}{l}CH_3\\CH_3\end{array}\!\!>CH.CH_2.C(OH)\!<\!\begin{array}{l}CH_3\\CH_3\end{array}$, is produced by action of zinc methyl on valeryl chloride. It is a colourless liquid, of camphoraceous taste and smell, boils at 129°–131°, and yields acetic and isobutyric acids on oxidation.



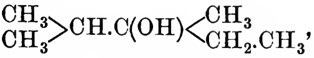
Diisopropyl carbinol, $\begin{array}{l}CH_3\\CH_3\end{array}\!\!>CH.CH(OH).CH\!<\!\begin{array}{l}CH_3\\CH_3\end{array}$, prepared by action of nascent hydrogen on diisopropyl ketone, is a liquid of pleasant ethereal odour, boiling at 131°–132° and of sp. gr. ·8593 at 0°.



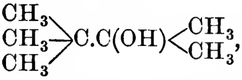
Propyl-ethyl-methyl carbinol, $\begin{array}{r}CH_3.CH_2\\CH_3.CH_2.CH_2\\CH_3\end{array}\!\!>C.OH$, prepared by the successive actions of zincic methide and ethide and water on normal butyric chloride, boils at 135°–138°.



Triethyl carbinol, $\begin{array}{l}CH_3.CH_2\\CH_3.CH_2\end{array}\!\!>C(OH).CH_2.CH_3$, is obtained by the action of propionic chloride, $(CH_3.CH_2.CO.Cl)$, upon zinc ethyl. It boils at 140°–142°, and is viscid at $-20°$.



Isopropyl-ethyl-methyl carbinol, $\begin{array}{l}CH_3\\CH_3\end{array}\!\!>CH.C(OH)\!<\!\begin{array}{l}CH_3\\CH_2.CH_3\end{array}$, is obtained by the successive actions of zincic ethide and methide and of water on isobutyric chloride. It boils at 124°–127°.



Trimethyl-carbin-dimethyl carbinol, $\begin{array}{l}CH_3\\CH_3\\CH_3\end{array}\!\!>C.C(OH)\!<\!\begin{array}{l}CH_3\\CH_3\end{array}$, is obtained by the successive actions of zincic methide and water on trimethacetic chloride. It forms long needles, melting at 17°, and boils at 123°–132°.

Octylic Alcohols, $C_8H_{18}O$ or $C_8H_{17}.OH$.

173. The ethereal oil of *Heracleum spondylium* consists mainly of the acetate (boiling at 206°–208°) of *primary normal octylic alcohol*, $CH_3.CH_2.CH_2.CH_2.CH_2.CH_2.CH_2.CH_2.OH$. The same body is contained, along with hexylic butyrate, in the oil of *Heracleum giganteum.* The alcohol obtained by saponification with potash boils at 190°–192°, has sp. gr. ·83 at 16° and a peculiar penetrating odour.

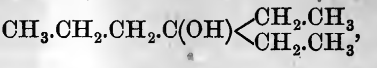
Methyl-hexyl carbinol, or *a normal secondary octylic alcohol :*

$$CH_3.CH_2.CH_2.CH_2.CH_2.CH_2.CH(OH).CH_3,$$

is obtained from the distillation of castor oil with potassic hydrate, and from the first chlor-substitution products of normal octane. It is an oily liquid, boiling at 181°, and yields by oxidation first methyl-hexyl ketone and later acetic and caproic acids.

Ethyl-isoamyl carbinol, $CH_3.CH_2.CH(OH).CH_2.CH_2.CH\!<\!\begin{array}{l}CH_3\\CH_3\end{array}$, boils at 182°–186°.

Diethyl-propyl carbinol:



$$CH_3.CH_2.CH_2.C(OH)\!<\!\begin{matrix}CH_2.CH_3\\CH_2.CH_3\end{matrix},$$

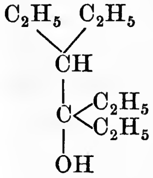
is a tertiary alcohol prepared by the action of zinc ethyl upon butyric chloride. It is not yet known quite pure, but boils between 145° and 155°.

Nonylic Alcohol, $C_9H_{20}O$ or $C_9H_{19}.OH$.

174. At present there is only a single body of this formula known; it is prepared from petroleum nonane, boils at about 200°, and is probably *methyl-heptyl carbinol.*

Decatylic Alcohol, $C_{10}H_{22}O = C_{10}H_{21}.OH$.

175. The only alcohol of this formula known with any certainty is that obtained by action of zinc ethyl upon bromacetic bromide, and has probably the constitutional formula:



Its boiling point is very low—namely, 155°–157°.

176. Alcohols of the formulæ

$$C_{11}H_{24}O,\ C_{12}H_{26}O,\ C_{13}H_{28}O,\ C_{14}H_{30}O, \text{ and } C_{15}H_{32}O$$

have not yet been prepared, but there are some higher, naturally occurring members of the series known; about whose constitution nothing is ascertained.

177. *Cetylic alcohol,* or *ethal,* $C_{16}H_{34}O = C_{16}H_{33}.OH$, is prepared from spermaceti (cetylic palmitate) by long boiling with alcoholic potassic hydrate:

$$C_{16}H_{33}.O.C_{16}H_{31}O + KOH = C_{16}H_{33}OH + KO.C_{16}H_{31}.O.$$

After the action is finished, the cetylic alcohol is precipitated by addition of water (in which potassic palmitate is soluble) and purified by crystallisation from alcohol.

Ethal so obtained crystallises in leaves, fuses at 49°–50°, and by careful heating, best in a stream of gas, can be slowly volatilised. It is completely insoluble in water.

178. *Cerylic alcohol,* $C_{27}H_{56}O = C_{27}H_{55}.OH$, forms as its cerotate the chief constituent of Chinese wax, from which it can be prepared in manner similar to that of cetylic alcohol from spermaceti. It is more usual to fuse the Chinese wax with potassic hydrate containing a little water:

$$C_{27}H_{55}.O.C_{27}H_{53}O + KOH = C_{27}H_{55}.OH + C_{27}H_{51}O.OK,$$

and to then extract the potassic cerotate from the cooled mass with water. The undissolved cerylic alcohol is then purified by crystallisation from ether. It fuses at 79° and solidifies on cooling to a wax-like mass.

179. *Mellissylic* or *myricylic alcohol*, $C_{30}H_{62}O$ or $C_{30}H_{61}.OH$. That portion of bees' wax insoluble in boiling alcohol, consists of mellissylic palmitate, $C_{30}H_{61}.O.C_{16}H_{31}O$, which, by similar treatment to that above given for spermaceti and Chinese wax, yields mellissylic alcohol. It is crystallisable, and fuses at 88°. One of its salts also occurs in the wax-like surface of the leaves of *Copernica cerifera*, the so-called carnuba wax.

HALOID COMPOUNDS OF THE ALCOHOL RADICALS.

Formation.

180. As already mentioned, the halogen compounds of the monovalent alcohol radicals can be partly prepared from the paraffins by direct substitution of a hydrogen atom by a halogen atom; but, as fluorine is unknown in the free state, and as iodine acts upon them with little energy, this method of preparation from the hydrocarbons is reduced to one for chlorides and bromides only. The procedure has been already given.

The alcohols are the materials generally employed in the preparation of these bodies.

The reaction is analogous to the conversion of metallic hydrates into halogen compounds by action of the haloid acids:

$$C_nH_{2n+1}.OH + HF = C_nH_{2n+1}F + H_2O$$
$$C_nH_{2n+1}.OH + HCl = C_nH_{2n+1}Cl + H_2O$$
$$C_nH_{2n+1}.OH + HBr = C_nH_{2n+1}Br + H_2O$$
$$C_nH_{2n+1}.OH + HI = C_nH_{2n+1}I + H_2O$$

The usual method is as follows: the alcohol, rendered as anhydrous as possible, is saturated with the gaseous acid (of which it is a very powerful absorbent), the reaction being assisted by the application of heat, and the mixture then separated by fractional distillation, if the boiling points of the alcohol and haloid salt permit; or if the alcohol be soluble in water, and the haloid salt insoluble, this latter can be precipitated by addition of water, separated mechanically from the aqueous alcoholic layer, and purified by distillation.

Instead of preparing the acid gases in other vessels, and then conducting them into the alcohol, the preparation and action are often conveniently combined. By gently heating an alcohol with common salt and sulphuric acid, there results, e.g., an alcoholic chloride:

$$C_nH_{2n+1}.OH + NaCl + H_2SO_4 = C_nH_{2n+1}Cl + NaHSO_4 + H_2O.$$

The equation given expresses the reaction of the ingredients—so far as they ensue—truly, but the number of reacting molecules by no means corresponds to the whole mass employed. An equal number of molecules of alcohol and haloid acid, brought into reaction, yield under no circumstances the same number of molecules of new products, as in every case a certain number of the ingredient molecules remain unchanged. The true result is therefore expressed according to the following equation:

$$aC_nH_{2n+1}.OH + aHCl = bC_nH_{2n+1}Cl + bH_2O$$
$$+ (a-b)C_nH_{2n+1}.OH + (a-b)HCl,$$

wherein the relative values of *a* and *b* depend on the one hand on the amount of affinity, on the other on the temperature. The relative proportion of the ingredients at starting has also an essential influence on the yield, i.e. the relative quantities of the end products. If it is desired, for instance, to convert as much as possible of the alcohol employed into the haloid salt, it is needful to bring as much acid as possible into the reaction; this latter, however, would be itself more completely converted if the alcohol were in large excess.

The conversion of an alcohol into the haloid salt is effected far more readily by use of the haloid compounds of sulphur or phosphorus, instead of the haloid acids, as these exchange halogen for oxygen or hydroxyl, with much greater readiness than is the case with the hydrogen haloids. The phosphorus haloids generally are employed, of which the pentachloride and pentabromide react very completely; e.g.

$$PCl_5 + C_nH_{2n+1}.OH = C_nH_{2n+1}.Cl + POCl_3. + HCl.$$

The phosphorus compounds give up the whole of the halogen easily, so that larger quantities of the alcohols can be attacked:

$$PCl_5 + 4C_nH_{2n+1}.OH = PO(OH_3) + HCl + 4C_nH_{2n+1}Cl,$$

the haloid acid also being able to act on further quantities of the alcohol; but by so working a large quantity of the alcohol is invariably lost, as far as the intended conversion into haloid is concerned, the phosphoric acid formed attacking the alcohol with formation of ethereal phosphates and at the same time of water, whose presence prevents the completion of the desired reaction.

The same objections apply to the use of phosphorous trichloride, that leading to the formation of phosphites and water.

A simple method, especially for the preparation of secondary and tertiary iodides, consists in the addition of the elements of the haloid acids to the olefines, the hydrocarbons of the series C_nH_{2n}, of which method frequent mention has already been made (§ 163, &c.)

General Properties.

181. The haloid compounds of the alcohol radicals are without exception colourless, generally agreeable-smelling liquids, far less soluble in water than the corresponding alcohols. They are miscible with alcohol in every proportion. By water they are decomposed to some extent, the reaction being the reverse to that of their formation:

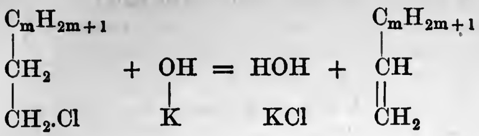
$$aC_nH_{2n+1}Cl + bHOH = cC_nH_{2n+1}.OH$$
$$+ cHCl + (a-c)C_nH_{2n+1}.Cl + (b-c)H_2O.$$

The reaction can be rendered nearly complete by employing the water in very large excess, and assisting the reaction by heat.

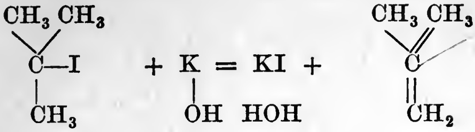
The alkalies—best in alcoholic solution—act more energetically than water on these salts, the alcohol being thereby partly regenerated:

$$C_nH_{2n+1}Cl + KOH = KCl + C_nH_{2n+1}.OH.$$

But to a much greater extent the hydroxyl of the alkaline hydrates acts as an oxidising agent, and, instead of attaching itself to the carbon, removes the hydrogen atom from the neighbouring carbon atom, with formation of water and an olefine:



$$\begin{array}{l} C_mH_{2m+1} \\ | \\ CH_2 \\ | \\ CH_2.Cl \end{array} + \begin{array}{c} OH \\ | \\ K \end{array} = \begin{array}{c} HOH \\ \\ KCl \end{array} + \begin{array}{l} C_mH_{2m+1} \\ | \\ CH \\ \| \\ CH_2 \end{array}$$



Usually and most completely the alcoholic iodides are reconverted into the alcohols by treatment with moist freshly precipitated argentic oxide:

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

still better by heating with potassic acetate and subsequent saponification with alkali (§ 163).

182. The alcoholic haloid salts can be reconverted into the paraffins by treatment with nascent hydrogen, especially in presence of strongly positive metals; the iodides, in addition, by heating with concentrated hydriodic acid (§ 149) or with zinc and water:

$$\begin{aligned} C_nH_{2n+1}Cl + Zn + HCl &= C_nH_{2n+2} + ZnCl_2 \\ C_nH_{2n+1}I + HI &= C_nH_{2n+2} + I_2 \\ 2C_nH_{2n+1}I + 2Zn + 2OH_2 &= 2C_nH_{2n+2} + ZnI_2 + Zn(OH)_2. \end{aligned}$$

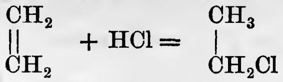
The fluorides of the alcohol radicals, formed by passing hydrofluoric acid into the alcohols, are scarcely known.

Chlorides of the Alcohol Radicals, $C_nH_{2n+1}Cl$.

183. *Methylic chloride*, or *monochlormethane*, $CH_3.Cl$, is readily obtained as a colourless gas, by slightly heating a mixture of one part of wood spirit with two parts of sodic chloride and three parts of concentrated sulphuric acid; it is purified by washing with water, then dried by passing over calcic chloride, and finally passed into vessels cooled by immersion in a mixture of ice and crystallised calcic chloride, wherein it condenses to a colourless mobile liquid, whose boiling point is −24° to −22°. Methylic chloride possesses an agreeable ethereal odour and a sweet taste; its vapour density is 1·736; it is soluble in $\frac{1}{4}$ of its volume of water and $\frac{1}{35}$ of its volume of alcohol. With chlorine in diffused daylight it yields further substitution products:

$$CH_2Cl_2,\ CHCl_3, \text{ and } CCl_4.$$

184. *Ethylic chloride, monochlorethane*, $C_2H_5Cl = CH_3.CH_2Cl$. It is prepared either by distilling alcohol with double its weight of sodic chloride and sulphuric acid, or by saturating well-cooled absolute alcohol with hydrochloric acid gas, letting the mixture stand some days in well-closed vessels, and then distilling on a water bath; the evolved vapours are washed with luke-warm water, dried by calcic chloride, and condensed in vessels cooled below 0°. The reaction in this and analogous cases is much facilitated, and rendered more complete, by the presence of powerful dehydrating agents, especially by zincic chloride. It also results from the continued heating of a gaseous mixture of ethylene and hydrochloric acid :



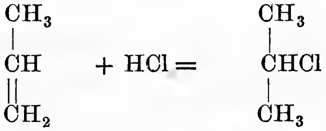
$$\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} + HCl = \begin{matrix} CH_3 \\ | \\ CH_2Cl \end{matrix}$$

Ethylic chloride is an extremely volatile, colourless liquid, of sp. gr. ·9214 at 0°, boiling at 11°–12°. It is readily inflammable, and burns, like all chlorine compounds, with a green-bordered flame. It is little soluble in water (in 50–60 parts), but in all proportions in absolute alcohol. With chlorine in daylight it gives higher substitution products : $C_2H_4Cl_2$, $C_2H_3Cl_3$, $C_2H_2Cl_4$, C_2HCl_5, and finally C_2Cl_6.

185. Two *propylic chlorides* are known corresponding to the formula C_3H_7Cl.

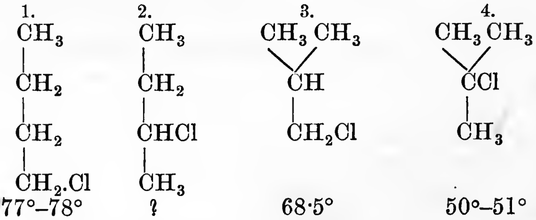
Normal propylic chloride, $CH_3.CH_2.CH_2Cl$, is obtained from normal propylic alcohol, in manner similar to the above, as a liquid nearly insoluble in water, boiling at 46·5°.

Secondary or *isopropylic chloride*, $CH_3.CHCl.CH_3$, obtained from isopropylic alcohol, boils at 36°–38°. It is also formed by union of hydrochloric acid with propylene gas :



$$\begin{matrix} CH_3 \\ | \\ CH \\ \| \\ CH_2 \end{matrix} + HCl = \begin{matrix} CH_3 \\ | \\ CHCl \\ | \\ CH_3 \end{matrix}$$

186. *Butylic chlorides*, C_4H_9Cl. Four isomers of this formula exist, corresponding to the four butylic alcohols, from which they are generally prepared. They are :



	1.	2.	3.	4.
Boiling point	77°–78°	?	68·5°	50°–51°
Sp. gr. .	·894		·8789	
	Primary	Secondary	Primary	Tertiary
	Normal butylic chlorides.		Isobutylic chlorides.	

187. Of the higher homologues it will suffice to mention

Primary normal amylic chloride, $CH_3.CH_2.CH_2.CH_2.CH_2.Cl$, boiling at 106°–107°.

Primary isoamylic chloride, ${CH_3 \atop CH_3}\!>\!CH.CH_2.CH_2.Cl$, boiling at 102°.

The boiling point of the *normal primary hexylic chloride*, $CH_3.CH_2.CH_2.CH_2.CH_2.CH_2Cl$, prepared from hexane, is 125°–128°.

Normal primary octylic chloride boils at 180·5°, and has sp. gr. ·8802 at 16°.

Cetylic chloride, $C_{16}H_{33}Cl$, is a liquid which cannot be distilled without decomposition.

Bromides of the Alcohol Radicals, $C_nH_{2n+1}.Br$.

188. The bromine compounds of the alcohol radicals are mostly prepared by action of phosphoric bromide on the alcohols. Instead of first preparing that body in the pure state, and then bringing it in contact with the alcohol, it is more convenient to pour over one part of amorphous phosphorus six times its weight of the alcohol, and then to add slowly about six parts of bromine with continued shaking and careful cooling. The bromide is separated from the alcohol by distillation.

Methylic bromide, CH_3Br, is a colourless liquid, boiling at + 13°, of sp. gr. 1·664 and of vapour density 3·293.

Ethylic bromide, C_2H_5Br, boils at 39° and has sp. gr. 1·4.

Propylic bromides:

Normal propylic bromide, $CH_3.CH_2.CH_2Br$, boils at 71° and has at 0° sp. gr. 1·388.

Isopropylic bromide, $CH_3.CHBr.CH_3$, of sp. gr. 1·32 at 13°, boils at 60°–63°.

Of the *butylic bromides*, C_4H_9Br, there are known the *normal primary*, $CH_3.CH_2.CH_2.CH_2Br$, of sp. gr. 1·305 at 0°, and of boiling point 100°–100·5°; and

Primary isobutylic bromide,  $\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right>CH.CH_2Br$, which boils at 92°.

Amylic bromides, $C_5H_{11}Br$:

Normal primary amylic bromide, $CH_3.CH_2.CH_2.CH_2.CH_2Br$, boils at 128·7°, and has sp. gr. 1·246 at 0°.

Primary isoamylic bromide,  $\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right>CH.CH_2.CH_2Br$, boils at 119°.

Secondary isoamylic bromide,  $\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right>CH.CHBr.CH_3$, at 113°; it is obtained from isoamylene by heating with hydrobromic acid.

Higher homologues are little known; of them only *normal primary octylic bromide*, a liquid boiling at 198°–200°, is worth mention.

Iodides of the Alcohol Radicals, $C_nH_{2n+1}I$.

189. The iodides of the alcohol radicals can all be prepared from the corresponding alcohols; the usual method is exactly the same as that given for the bromides. It consists in placing one part of amorphous phosphorus in five to ten parts of the alcohol, and distilling after addition of ten parts of iodine.

Instead of amorphous phosphorus the ordinary modification can be employed; the method of proceeding will be described under ethylic iodide.

Secondary and such tertiary iodides as have the iodine in union with a carbon atom which is attached to a CH_3 group, can be prepared from the respective olefines (C_nH_{2n}) by heating with concentrated hydriodic acid (§ 163). At higher temperatures the secondary compounds easily decompose again into the olefine and hydriodic acid.

All these iodides turn brown on exposure to light, from separation of iodine, a paraffin being formed at the same time:

$$2C_nH_{2n+1}I = I_2 + C_nH_{2n+2}.$$

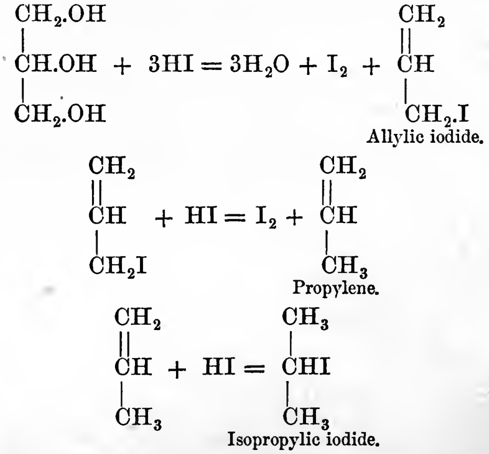
190. *Methylic iodide*, CH_3I, is a colourless, sweet-smelling liquid, nearly insoluble in water, boils at 44°–45°, and has sp. gr. 2·199.

191. *Ethylic iodide*, $CH_3.CH_2I$, can be prepared as follows: A mixture of one part phosphorus with four parts absolute alcohol is placed in a retort connected with an inverted condenser, and ten parts of iodine, either solid or dissolved in alcohol, gradually added. Phosphorous iodide is formed with evolution of heat, which immediately reacts on the alcohol, the liquid generally entering into spontaneous ebullition. It is finally gently heated on the water bath for an hour, and the product distilled off. The distillate is then shaken with water to remove alcohol, and the separated iodide dried over calcic chloride and distilled.

Ethylic iodide is a colourless, strongly refractive liquid of pleasant sweetish taste, of sp. gr. 1·946 at 16° and boiling at 72°.

192. *Propylic Iodides.—Normal propylic iodide*, $CH_3.CH_2.CH_2.I$, has sp. gr. 1·782 at 0° and boils at 102°.

Isopropylic iodide, $CH_3.CHI.CH_3$, is usually prepared from glycerine by means of iodine and amorphous phosphorus. Propylene and allylic iodide are formed and are converted into isopropylic iodide by excess of hydriodic acid:



$$\begin{array}{l}CH_2.OH\\ |\\ CH.OH\\ |\\ CH_2.OH\end{array} + 3HI = 3H_2O + I_2 + \begin{array}{l}CH_2\\ \|\\ CH\\ |\\ CH_2.I\end{array}$$

Allylic iodide.

$$\begin{array}{l}CH_2\\ \|\\ CH\\ |\\ CH_2I\end{array} + HI = I_2 + \begin{array}{l}CH_2\\ \|\\ CH\\ |\\ CH_3\end{array}$$

Propylene.

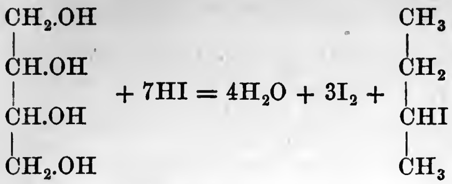
$$\begin{array}{l}CH_2\\ \|\\ CH\\ |\\ CH_3\end{array} + HI = \begin{array}{l}CH_3\\ |\\ CHI\\ |\\ CH_3\end{array}$$

Isopropylic iodide.

It boils at 89° and has at 0° sp. gr. 1·735; it is not miscible with water.

193. *Butylic Iodides*, C_4H_9I.—*Normal primary butylic iodide*, $CH_3.CH_2.CH_2.CH_2I$, obtained from the normal primary alcohol, boils at 129°, and has sp. gr. 1·643 at 0°.

Normal secondary butylic iodide, $CH_3.CH_2.CHI.CH_3$, results, by a similar reaction to that for isopropylic iodide, by heating erythrite with hydriodic acid:



$$\begin{array}{l}CH_2.OH\\ |\\ CH.OH\\ |\\ CH.OH\\ |\\ CH_2.OH\end{array} + 7HI = 4H_2O + 3I_2 + \begin{array}{l}CH_3\\ |\\ CH_2\\ |\\ CHI\\ |\\ CH_3\end{array}$$

It boils at 117°–118°, and has sp. gr. 1·6 at 20°. It is converted into the normal secondary alcohol by treatment with moist argentic oxide.

Primary isobutylic iodide, $\begin{array}{l}CH_3\\ CH_3\end{array}\!\!>CH.CH_2I$, obtained from fermentation butylic alcohol, has sp. gr. 1·592 at 22°, and boils at 120·5°.

Tertiary isobutylic iodide, or *trimethyl-carbin iodide:*

$$\begin{array}{l}CH_3\\ CH_3\end{array}\!\!>CI—CH_3,$$

is most easily prepared from isobutylene and hydriodic acid. Its boiling point is 99°.

194. *Amylic Iodides.—Normal primary amylic iodide:*

$$CH_3.CH_2.CH_2.CH_2.CH_2I,$$

boils at 155°; sp. gr. 1·5435 at 0°.

a Normal secondary amylic iodide, $CH_3.CH_2.CH_2.CHI.CH_3$, boils at 146°.

a Primary isoamylic iodide, $\begin{array}{l}CH_3\\ CH_3\end{array}\!\!>CH.CH_2.CH_2I$, fermentation amylic iodide, prepared from fusel oil, boils at 147°, and has sp. gr. 1·511 at 11°.

Secondary isoamylic iodide, $\begin{array}{l}CH_3\\ CH_3\end{array}\!\!>CH.CHI.CH_3$, prepared from isoamylene and hydriodic acid, boils at 128°–130°.

195. *Hexylic Iodides.—Normal primary hexylic iodide:*

$$CH_3.CH_2.CH_2.CH_2.CH_2.CH_2I.$$

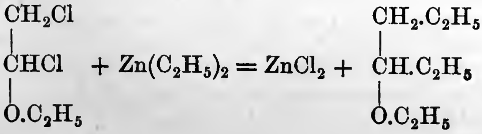
Boiling point 179·5; sp. gr. 1·4115 at 17·5°.

a Normal secondary hexylic iodide, $CH_3.CH_2.CH_2.CH_2.CHI.CH_3$, prepared from mannite and hydriodic acid:

$$C_6H_8(OH)_6 + 11HI = 6H_2O + 5I_2 + C_6H_{13}I,$$

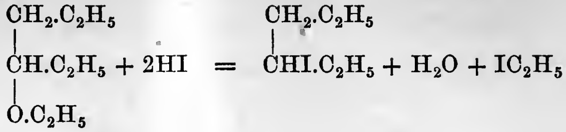
boils at 167·5°, and has sp. gr. 1·4477 at 0°.

β Normal secondary hexylic iodide, $CH_3.CH_2.CH_2.CHI.CH_2.CH_3$, is prepared by heating the product of the reaction of bichlorether upon zinc ethyl:



$$\begin{array}{l}CH_2Cl\\ |\\ CHCl\\ |\\ O.C_2H_5\end{array} + Zn(C_2H_5)_2 = ZnCl_2 + \begin{array}{l}CH_2.C_2H_5\\ |\\ CH.C_2H_5\\ |\\ O.C_2H_5\end{array}$$

with hydriodic acid:



$$\begin{array}{l} CH_2.C_2H_5 \\ | \\ CH.C_2H_5 \\ | \\ O.C_2H_5 \end{array} + 2HI = \begin{array}{l} CH_2.C_2H_5 \\ | \\ CHI.C_2H_5 \end{array} + H_2O + IC_2H_5$$

It is a liquid of high boiling point.

The iodide of primary fermentation hexylic alcohol, probably $\begin{array}{l} CH_3 \\ CH_3 \end{array}\!\!>CH.CH_2.CH_2.CH_2I$, distils between 172° and 175°.

196. Of the higher homologues may be mentioned

Normal primary octylic iodide:

$$CH_3.CH_2.CH_2.CH_2.CH_2.CH_2.CH_2.CH_2I,$$

boiling at 220°–222°.

Cetylic iodide, $C_{16}H_{33}I$, prepared from cetylic alcohol by means of phosphoric iodide, is a solid body, which, after recrystallisation from alcohol, fuses at 22°.

METALLIC ALCOHOLATES, $C_nH_{2n+1}.OM$.

197. The hydroxylic hydrogen of alcohols is only replaced directly, with evolution of hydrogen gas, by the most strongly positive metals, and then always with less energy than in the action of the metal upon water. The metallic alcoholates so formed are solid bodies, in great part readily soluble in alcohol, are capable of standing high temperatures without decomposition, but are very readily decomposed by water. If a metallic alcoholate be treated with water, it is converted into hydrate, with considerable evolution of heat. Unless, however, the water be in great excess the decomposition is not complete, and can be represented by the general equation:

$$xC_nH_{2n+1}.ONa + xHOH = yC_nH_{2n+1}.OH + yNaOH \\ + (x-y)C_nH_{2n+1}ONa + (x-y)HOH,$$

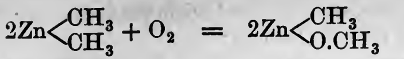
in which y, by employment of equal molecules of the ingredients, is invariably considerably greater than $\frac{1}{2}x$.

The decomposition is naturally diminished by addition of alcohol, as in reverse action, on bringing together the strongest metallic bases and alcohols, some amount of metallic alcoholates are formed:

$$xKOH + yC_nH_{2n+1}.OH = zC_nH_{2n+1}.OK + zH_2O + (x-z)KOH \\ + (y-z)C_nH_{2n+1}.OH.$$

The alcoholates can never be obtained pure by this last reaction; but their formation is placed beyond doubt by some of the reactions of the solutions of strong metallic hydrates in absolute alcohol, as, for instance, the formation of metallic alkylic carbonates on passing carbonic anhydride.

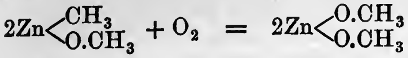
These compounds are scarcely known in the case of the heavy metals, except those of aluminium and zinc, which latter result from the slow oxidation of zinc alkyls by atmospheric oxygen:



$$2\mathrm{Zn}<\begin{matrix}CH_3\\CH_3\end{matrix} + O_2 = 2\mathrm{Zn}<\begin{matrix}CH_3\\O.CH_3\end{matrix}$$

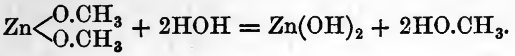
Zinc dimethyl. Zinc methyl methylate.

and



$$2\mathrm{Zn}<\begin{matrix}CH_3\\O.CH_3\end{matrix} + O_2 = 2\mathrm{Zn}<\begin{matrix}O.CH_3\\O.CH_3\end{matrix}$$

as solid bodies, readily converted by water into alcohols with separation of zincic hydrate:



$$\mathrm{Zn}<\begin{matrix}O.CH_3\\O.CH_3\end{matrix} + 2HOH = Zn(OH)_2 + 2HO.CH_3.$$

They are decomposed by acids and halogen compounds with still greater readiness than by water.

The best known member of the series is

198. *Sodic ethylate,* $C_2H_5.O.Na = CH_3.CH_2.O.Na$. This is readily obtained by placing one part of bright metallic sodium in ten parts of quite anhydrous alcohol. Hydrogen is given off violently, and so much heat is evolved that either the vessel must be cooled or else the metal added in small quantities and slowly. The whole of the alcohol cannot be converted into its sodium derivative by this means. In order to obtain a pure product, when all action has ceased, the excess of alcohol is removed by distillation from a water bath; a white crystalline mass remains, which is a compound of one molecule of sodic ethylate with two molecules of alcohol, $C_2H_5.ONa,2C_2H_5.OH$. Either by long exposure in a vacuum or by heating to 200° in a current of hydrogen, this compound is resolved into alcohol, which volatilises, and a white, very voluminous residue of sodic ethylate, $C_2H_5.ONa$, which is not decomposed by a temperature of 290°.

ETHERS OR OXIDES OF THE ALCOHOL RADICALS.

$$C_nH_{2n+1}.O.C_nH_{2n+1} \text{ and } C_nH_{2n+1}.O.C_mH_{2m+1}.$$

199. The ethers are compounds of two alcohol radicals with one oxygen atom; they can be regarded as alcohols whose hydroxylic hydrogen atom has been replaced by an alcohol radical. They can be divided into two groups, the first or *simple ethers* containing two similar alcohol radicals, whilst in the second, the so-called *mixed ethers,* two dissimilar alcohol radicals are united together by oxygen. In this way many more ethers are possible than alcohols. The general formula of the ethers:

$$C_nH_{2n+1}.O.C_mH_{2m+1} = C_{n+m}H_{2(n+m)+2}O = C_{n'}H_{2n'+2}O \text{ (if }_{n+m=n'}),$$

being identical with that of the alcohols, numerous cases of metamerism must occur between members of the two classes of bodies.

200. *Methods of Preparation.*—All ethers can be prepared by action of metallic alcoholates upon the haloid compounds of the alcohol radicals. Of the first the sodium compounds are best employed; of the last, the easily decomposable iodides; the action then starting without application of heat, but can be accelerated and finished by heating.

If a sodic alcoholate be heated with the iodide of the same alcohol radical, a simple ether is formed:

$$C_nH_{2n+1}.ONa + IC_nH_{2n+1} = NaI + C_nH_{2n+1}.O.C_nH_{2n+1}$$
$$\text{or } (C_nH_{2n+1})_2O;$$

whilst the derivatives of different alcohol radicals give mixed ethers, it being, as regards the end product, a matter of indifference which alcohol radical is employed as the sodium oxyderivative and which as the haloid salt:

$$C_nH_{2n+1}.ONa + IC_mH_{2m+1} = NaI + C_nH_{2n+1}.O.C_mH_{2m+1},$$
$$\text{or } C_nH_{2n+1}.I + C_mH_{2m+1}.ONa = NaI + C_nH_{2n+1}.O.C_mH_{2m+1}.$$

As a rule the sodic alcoholate is not employed pure, but dissolved in an excess of the alcohol. The ether must in every case be purified by distillation.

The only cases where good yields are obtained by this process are the mixed methyl ethers, prepared from methylic iodide and sodic alcoholates; the higher homologous iodides so reacting with the alcoholates as in great part to produce olefines:

$$C_nH_{2n+1}I + NaO.C_mH_{2m+1} = NaI + HO.C_mH_{2m+1} + C_nH_{2n}.$$

Those salts of alcohol radicals with acids, which are not volatile without decomposition, and better the acid than the neutral salts, yield ethers and free acids when heated with alcohol to high temperatures:

$$C_nH_{2n+1}.HSO_4 + C_nH_{2n+1}.OH = H_2SO_4 + (C_nH_{2n+1})_2O$$

and

$$C_nH_{2n+1}.HSO_4 + C_mH_{2m+1}.OH = H_2SO_4 + C_nH_{2n+1}.O.C_mH_{2m+1}.$$

Monethylic sulphate, for instance, when heated with ethylic alcohol to about 140°, decomposes into diethylic oxide and sulphuric acid:

$$C_2H_5.HSO_4 + C_2H_5.OH = H_2SO_4 + (C_2H_5)_2O.$$

The simple ethers can also be prepared by heating the haloid compounds of the alcohol radicals with the anhydrous oxides of basic metals, most readily by employment of iodides and argentic oxide:

$$2C_nH_{2n+1}I + Ag_2O = Ag_2I_2 + (C_nH_{2n+1})_2O.$$

The method most frequently employed for preparing the simple ethers consists in heating the respective alcohols with sulphuric acid. Bearing in mind only the ingredients and the final products, the reaction may be represented by the equation:

$$2C_nH_{2n+1}.OH + H_2SO_4 = (C_nH_{2n+1})_2O + H_2SO_4 + OH_2,$$

in which the process appears as the splitting off of a molecule of water, from two molecules of alcohol, by the dehydrating power of the sulphuric acid—a view which was formerly held. As a matter of fact it is quite different, being essentially the same as the second method mentioned above. During the preparation of ether by heating an alcohol with sulphuric acid, it is found that water distils over *before* the ether, although the latter may have a lower boiling point; and, further, a very small quantity of sulphuric acid can decompose a very considerable quantity of alcohol. Both facts completely contradict the old view.

The formation of ether by this process belongs to the most intricate but at the same time most instructive chemical processes; it is therefore worth considering at some length.

201. *Preparation of Ethers from Alcohols and Sulphuric Acid.*—On mixing an alcohol with sulphuric acid, an acid sulphate of the alcohol radical is formed with evolution of heat. The process is by no means complete, the greater portion of both ingredients remaining unchanged:

$$aC_nH_{2n+1}.OH + bH_2SO_4 = xC_nH_{2n+1}.HSO_4 + xH_2O \\ + (a-x)C_nH_{2n+1}.OH + (b-x)H_2SO_4.$$

On applying heat, water and a part of the unaltered alcohol distil over, until the temperature reaches that at which ether is formed according to the second method (by the action of an alcohol on an acid sulphate), when ether occurs amongst the products distilling, and its formation continues as long as the liquid contains both alcohol and acid sulphate.

In the last phase of the process, as soon as, by the continued external application of heat, the temperature rises above that necessary for the formation of ether, and when the free alcohol is nearly exhausted, large quantities of an olefine are formed, due to the decomposition of the acid sulphate:

$$C_nH_{2n+1}HSO_4 = C_nH_{2n} + H_2SO_4.$$

As by these decompositions the sulphuric acid is regenerated and remains behind in the residue from the distillation, this latter can be used again and again for ether formation, the necessary fresh quantities of alcohol being added.

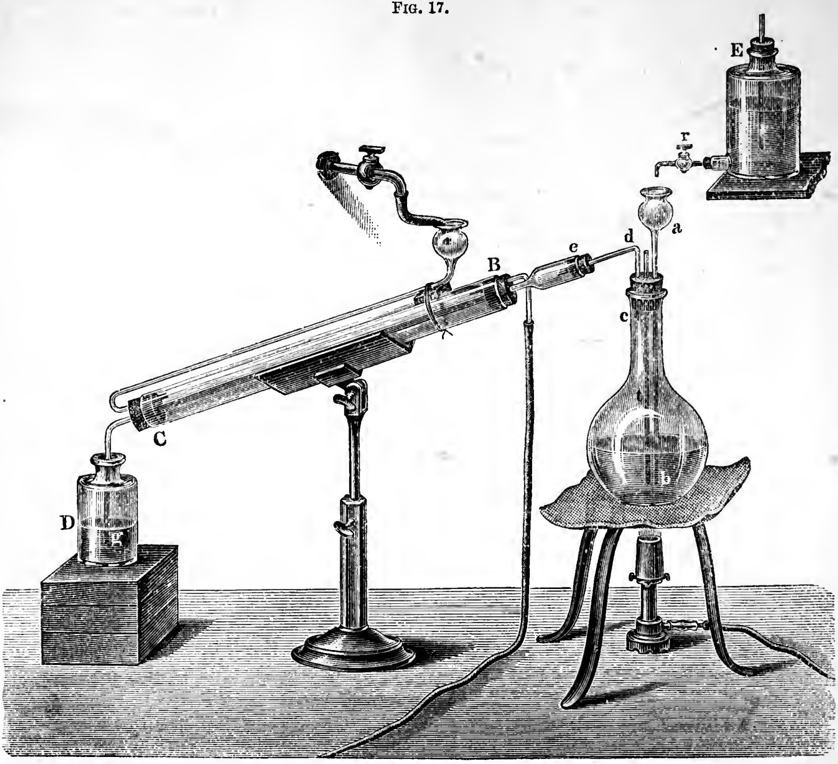
Instead of adding alcohol from time to time, the process may be made continuous. For this purpose the alcohol and sulphuric acid are mixed together in such proportions, that the mixture begins to boil at the temperature necessary for the formation of ether; alcohol is then allowed to flow continuously into the apparatus, at such a rate that a thermometer immersed in the liquid shows a constant temperature under the continued boiling; there is then as much alcohol passing into the vessel as distils from it in the same time, in the forms of ether, water, or unaltered alcohol.

Fig. 17 shows the apparatus used on the small scale. The flask, supported by a tripod stand over a gas flame, is provided with a triply bored cork; one opening contains the tube *d* leading to the condenser B; the second is for the thermometer *t*, which dips into the liquid; through the third a funnel tube passes, reaching nearly to the bottom of the flask. As soon as the boiling alcohol-acid mixture has reached the desired temperature, the cock *r* of the alcohol reservoir E is opened to such an extent that the amount of alcohol flowing down the funnel tube into the liquid shall keep the temperature at the same point.

The process might be interminable were it not that small quantities of the acid are changed in an unregenerable manner, there not only being a continual distillation of small quantities of organic compounds of sulphuric acid, but also oxidation occurs at the expense of the sulphuric acid, so that small quantities of sulphurous anhydride are always evolved.

The distillate collected in the receiver separates into two layers, the lower consisting mainly of water, the upper of ether. The latter is purified first by shaking with milk of lime, then repeatedly with fresh quantities of water, in order to remove any alcohol that may have passed over, and finally, after drying with calcic chloride, is submitted to fractional distillation.

FIG. 17.



Many other not readily volatile acids, such as phosphoric, arsenic, boric, &c., act in a similar manner to sulphuric acid.

202. Small quantities of ether are also obtained by heating the haloid compounds of alcohol radicals together with alcohols to 200° in sealed tubes :

$$xC_nH_{2n+1}Cl + yC_nH_{2n+1}.OH = z(C_nH_{2n+1})_2O + zHCl$$
$$+ (x-y)C_nH_{2n+1}Cl + (y-z)C_nH_{2n+1}.OH;$$

therefore also, together with alcohols, when the haloid salts are heated with water to 200°–250°. After the reaction :

$$xC_nH_{2n+1}Cl + yH_2O = zC_nH_{2n+1}.OH + zHCl + (x-z)C_nH_{2n+1}Cl + (y-z)H_2O,$$

follows further:

$$(x-z)C_nH_{2n+1}Cl + zC_nH_{2n+1}.OH + zHCl + (y-z)H_2O = t(C_nH_{2n+1})_2O + (z+t)HCl + (x-z-t)C_nH_{2n+1}Cl + (z-t)C_nH_{2n+1}.OH + (y-z)H_2O,$$

until a point of equilibrium is reached in the relative quantities of the ingredients and products. This point depends on the temperature, the quantities of the ingredients at starting, and the relative affinities coming into play.

The formation of ethers by strongly heating alcohols with chlorides, bromides, iodides, and neutral sulphates of weak basic metals, such as zinc, tin, mercury, aluminium, iron, uranium, &c., was formerly of special interest. It is known that nearly all these bodies, when heated to high temperatures with water, are partly decomposed into free acids and basic salts, especially when the acid can volatilise; for instance, $Al_2Cl_6 + 2H_2O = 4HCl + Al_2O_2Cl_2$. In every case these salts are more readily decomposed by alcohols, the negative constituent forming a compound with the alcohol radical. Zincic chloride heated with alcohol always yields some alcoholic chloride:

$$xZnCl_2 + yC_nH_{2n+1}.OH = zZn\begin{matrix}<^{Cl}_{OH}\end{matrix} + zC_nH_{2n+1}.Cl + (x-z)ZnCl_2 + (y-z)C_nH_{2n+1}.OH.$$

Normal aluminic sulphate yields a basic salt and acid sulphate of the alcohol radical, according to the equation:

$$xAl_2(SO_4)_3 + yC_nH_{2n+1}.OH = zAl_2(SO_4)(OH)_4 + 2zC_nH_{2n+1}.HSO_4 + (x-z)Al_2(SO_4)_3 + (y-2z)C_nH_{2n+1}.OH.$$

By the formation of haloid salts or sulphates of the alcohol radicals together with unchanged alcohol, all conditions necessary to the formation of ethers are given. The free acid thereby regenerated, probably assisted by the lowering of the temperature at the end of the reaction, converts the basic salt in great part back to the neutral compounds, so that it finally appears as though this latter had remained unaltered.

These reactions had been considered to be catalytic processes previously to the correct explanation of their action having been discovered.

203. If two alcohols are allowed to react simultaneously on the etherifying agent (sulphuric acid, &c.), three ethers are obtained, two simple and one mixed; sulphates, &c., of the two different alcohol radicals being formed, of which each reacts on each of the two alcohols, converting them into ethers.

These ethers are also obtained when a mixture of an alcohol and sulphuric acid is heated to the temperature of ether formation, and a second alcohol is allowed to flow in continuously. At the beginning only a single alcoholic sulphate is formed, which reacts with its unchanged alcohol, ($C_nH_{2n+1}.OH$), to form the ether, $(C_nH_{2n+1})_2O$, which is at first alone formed. If now the second alcohol, ($C_mH_{2m+1}.OH$), enters, it will form its acid sulphate with the still unaltered or regenerated sulphuric acid. This, reacting on the first alcohol, yields with it the ether, $(C_nH_{2n+1})(C_mH_{2m+1})O$. At the same time the same ether is formed by the action of the already formed molecules of $C_nH_{2n+1}.HSO_4$ on the second alcohol. In time the quantity formed of this second ether gradually increases, whilst that of the first ether soon diminishes. Soon, however, molecules of $C_mH_{2m+1}.OH$ come in contact with those of $C_mH_{2m+1}.HSO_4$, at first but seldom, later with increasing frequency. The second simple ether, $(C_mH_{2m+1})_2O$, therefore, begins to distil over in rapidly increasing quantity, forming at length the sole product; this occurring as soon as the first alcohol has completely distilled over in the form of $(C_nH_{2n+1})_2O$ and $C_nH_{2n+1}.O.C_mH_{2m+1}$.

204. *Properties and Reactions.*—The ethers are mostly liquids which distil unchanged, are either entirely insoluble or but little soluble in water. Their boiling points are invariably lower than those of the metameric alcohols. By reagents they are generally more difficultly attacked than the alcohols.

By water at high temperatures they are partly converted into alcohols; e.g.

$$a(C_2H_5)_2O + bH_2O = 2xC_2H_5.OH + (a-x)(C_2H_5)_2O + (b-x)H_2O.$$

By the halogen hydro-acids they are converted, on heating, into the haloid compounds of the alcohol radicals, most readily by hydriodic acid:

$$C_nH_{2n+1}.O.C_mH_{2m+1} + 2HI = C_nH_{2n+1}I + C_mH_{2m+1}I + H_2O,$$

and give salts with strong acids. Treated with chlorine, chlor-substitution products are readily obtained.

By oxidation, especially in presence of water, they yield essentially the same products as the alcohols from which they are derived, the ethers of primary alcohol radicals therefore giving aldehydes and acids.

205. *Methyl ether*, or *dimethylic oxide*, $C_2H_6O = CH_3.O.CH_3$ (metameric with ethylic alcohol). Methylic ether is obtained by distillation of a mixture of wood spirit with four times its weight of sulphuric acid; the evolved vapours are passed through potassic hydrate solution, and the unabsorbed gas condensed in vessels cooled by a powerful freezing mixture.

Methyl ether below $-21°$ is a mobile colourless liquid, at ordinary temperatures an ethereal-smelling gas, of density 1·617. 37 volumes of it are absorbed by one volume of water. It burns with a strongly luminous flame.

206. *Ethyl-methyl ether*, or *methylic ethylic oxide:*

$$C_3H_8O = CH_3.O.C_2H_5,$$

is prepared from sodic methylate and ethylic iodide, or better from methylic iodide and sodic ethylate, as a liquid boiling at + 11°. It is also formed, together with dimethylic oxide and ethyl ether, by heating a mixture of ethylic and methylic alcohols with sulphuric acid.

ETHYL ETHER.

207. *Ethyl ether, diethylic oxide,* also known as *ether* only, $C_4H_{10}O = C_2H_5.O.C_2H_5$. In order to prepare this 9 parts of strong sulphuric acid and 5 parts of 90 % alcohol are distilled at 140°, under constant addition of more alcohol, until the amount of the latter has reached about five times the weight of the sulphuric acid employed. The ethereal layer of the distillate, after repeated agitation with water, is dried by means of fused calcic chloride and then distilled. In order to obtain ether completely free from the last traces of alcohol, which adhere with great obstinacy, it must be allowed to stand over bright pieces of sodium until all evolution of hydrogen ceases.

Pure ether is a very mobile colourless liquid of penetrating odour, of sp. gr. ·736 at 0°, boils at 35°, and has vapour density 2·565. It is very inflammable, its vapour mixed with air being ignited by contact with platinum black, and burns with a luminous flame; a mixture of its vapour and air is violently explosive.

On account of its low boiling point, ether evaporates very quickly at ordinary temperatures, and causes thereby a great reduction of temperature.

It mixes in every proportion with absolute alcohol, but not with water; 1 part of ether requires about 9 parts of water for solution, and itself dissolves about $\frac{1}{11}$ of its weight of water. On shaking a mixture of equal volumes of water and ether, and then allowing to stand quietly, it rapidly separates into two layers, the under consisting of a solution of ether in water, the upper of water dissolved in ether. Ethylic ether dissolves about $\frac{1}{100}$ of its weight of sulphur and $\frac{1}{50}$ of phosphorus; it is one of the best solvents for fats, oils, resins, and other organic bodies, and dissolves many metallic haloid salts, such as auric chloride, platinic chloride, ferric chloride, mercuric chloride, &c.

A mixture of ethyl ether and dry bromine solidifies in a freezing mixture to a red crystalline compound, $(C_4H_{10}O)_2Br_6$, which is readily decomposed by water.

By incomplete oxidation or imperfect combustion it is converted into aldehyde and acetic acid. With hydrochloric acid it yields some ethylic chloride. It is not attacked by potassium or sodium, but is very energetically by chlorine, which causes a violent explosion, with separation of carbon, when mixed with ether vapour.

Chlor substitution products are obtained by passing chlorine in the dark through strongly cooled ether. The first formed are:

Monochlorether, C_4H_9ClO or $CH_3.CHCl.O.C_2H_5$ (boiling point 97°–98°); and *bichlorether,* $C_4H_8Cl_2O = CH_2Cl.CHCl.O.C_2H_5$, a liquid boiling with slight decomposition at about 145°, will be noticed at length further on. By further action of chlorine, which must be assisted by heating, bodies richer in chlorine are obtained, which on heating decompose with evolution of hydrochloric acid. Of these are known:

Trichlorether, $C_4H_7Cl_3O = CHCl_2.CHCl.O.C_2H_5$.

Tetrachlorether, $C_4H_6Cl_4O = CCl_3.CHCl.O.C_2H_5$, a thick liquid smelling like fennel; and

Pentachlorether, $C_4H_5Cl_5O = CCl_3.CCl_2.O.C_2H_5$.

If these bodies be heated, exposed to sun-light, and still further treated with chlorine, there is obtained as a final product

Perchlorether, $C_4Cl_{10}O = CCl_3.CCl_2.O.CCl_2.CCl_3$, which forms colourless crystals, melting at 69°, and decomposing at 300° into trichloracetyl chloride and perchlorethane:

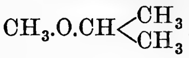
$$CCl_3.CCl_2.O.CCl_2.CCl_3 = \underbrace{CCl_3.COCl}_{\text{Trichloracetyl chloride.}} + \underbrace{CCl_3.CCl_3}_{\text{Perchlorethane.}}$$

The action of ethyl ether on the animal organism is noteworthy. It causes intoxication, or if breathed as vapour in large quantity it produces loss of consciousness and sensation. It is therefore employed as an anæsthetic.

208. Ethyl ether is metameric with *methyl-propyl ether:*

$$CH_3.O.CH_2.CH_2.CH_3,$$

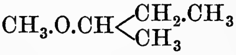
and *methyl-isopropyl ether*, $CH_3.O.CH<^{CH_3}_{CH_3}$. The first boils at 49°–52°.



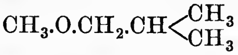
Of the ethers metameric with amylic alcohol, and containing five carbon atoms in the molecule ($C_5H_{12}O$), six have been prepared, namely:

Normal primary butyl-methyl ether, $CH_3.O.CH_2.CH_2.CH_2.CH_3$.

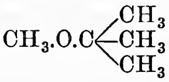
Normal secondary butyl-methyl ether, $CH_3.O.CH<^{CH_2.CH_3}_{CH_3}$



Primary isobutyl-methyl ether, $CH_3.O.CH_2.CH<^{CH_3}_{CH_3}$

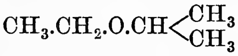


Tertiary isobutyl-methyl ether, $CH_3.O.C\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}$



Ethyl-propyl ether (boils at 85°–86°), $CH_3.CH_2.O.CH_2.CH_2.CH_3$.

Ethyl-isopropyl ether, $CH_3.CH_2.O.CH<^{CH_3}_{CH_3}$



209. The possible ethers metameric with the hexylic alcohols, $C_6H_{14}O$, are far more numerous than the foregoing, but few of them, however, are known.

Normal propyl ether, $CH_3.CH_2.CH_2.O.CH_2.CH_2.CH_3$, is a mobile liquid of ethereal odour, boiling at 86°.

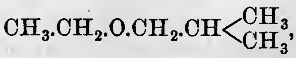
Isopropyl ether, ${}^{CH_3}_{CH_3}>CH.O.CH<^{CH_3}_{CH_3}$, a similar liquid, boils at 60°, and is obtained by decomposition of isopropylic iodide by argentic oxide.

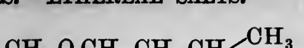
Normal primary butyl-ethyl ether:

$$CH_3.CH_2.O.CH_2.CH_2.CH_2.CH_3,$$

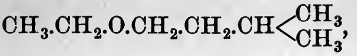
boils at 91·7°, and sp. gr. ·7694 at 0°.

Isobutyl-ethyl ether, $CH_3.CH_2.O.CH_2.CH<^{CH_3}_{CH_3}$, boils at 78°–80°.



Methyl-isoamyl ether,  $CH_3.O.CH_2.CH_2.CH<\genfrac{}{}{0pt}{}{CH_3}{CH_3}$, boils at 92°.

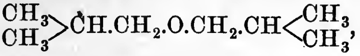
Higher homologues of the series are :—

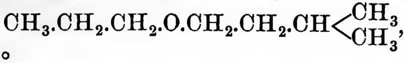
Ethyl-isoamyl ether,  $CH_3.CH_2.O.CH_2.CH_2.CH<\genfrac{}{}{0pt}{}{CH_3}{CH_3}$, boils at 112°.

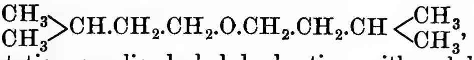
Normal primary butyl ether :

$$CH_3.CH_2.CH_2.CH_2.O.CH_2.CH_2.CH_2.CH_3,$$

boils at 140°–141°, and has at 0° sp. gr. ·784.

Isobutyl ether,  $\genfrac{}{}{0pt}{}{CH_3}{CH_3}>CH.CH_2.O.CH_2.CH<\genfrac{}{}{0pt}{}{CH_3}{CH_3}$, boils at 110°.

Propyl-isoamyl ether,  $CH_3.CH_2.CH_2.O.CH_2.CH_2.CH<\genfrac{}{}{0pt}{}{CH_3}{CH_3}$, distils between 125° and 130°.

Isoamyl ether,  $\genfrac{}{}{0pt}{}{CH_3}{CH_3}>CH.CH_2.CH_2.O.CH_2.CH_2.CH<\genfrac{}{}{0pt}{}{CH_3}{CH_3}$, prepared from fermentation amylic alcohol by heating with sulphuric acid, boils at 176°, and has sp. gr. about ·78.

Cetyl ether, $(C_{16}H_{33})_2O$, is prepared from sodic cetylate and cetylic iodide, the product being crystallised from ethylic ether. It forms glittering leaves, which melt at 55°, and distil at about 300° with slight decomposition.

THE ETHEREAL SALTS OR SO-CALLED COMPOUND ETHERS.

210. When alcohols and strong acids are mixed together, they react with elimination of water and formation of salts of the alcohol radicals. This reaction, even when assisted by heat, is invariably only partial, there always remaining certain quantities of unaltered alcohol and acid. The polybasic acids yield principally hydric salts corresponding to their hydric (or acid) metallic salts, which still act like acids, replacing their acid hydrogen by metals when added to metallic hydrates, &c.

A method of preparation frequently employable consists in heating the potassic or argentic salt of the acids with iodides of the alcohol radicals; e.g.

$$Ag_3PO_4 + 3C_nH_{2n+1}I = 3AgI + (C_nH_{2n+1})_3PO_4;$$

or by action of the acid chlorides on alcohols, or better on the sodic alcoholates :

$$SOCl_2 + 2NaO.C_nH_{2n+1} = 2NaCl + SO(OC_nH_{2n+1})_2.$$

All these compounds are partly decomposed into alcohol and acid by heating with water, and are readily and completely decomposed by heating with solution of strong basic hydrates, a metallic salt being formed and the alcohol liberated. The process is known as *saponification.*

In the following only the salts of the inorganic acids, of the cyanogen acids, and of carbonic acid will be given, those of the organic acids being mentioned later.

Nitrates of the Alcohol Radicals, $C_nH_{2n+1}.O.NO_2$.

211. The nitrates of the alcohol radicals result from the action of strong nitric acid on the alcohols; but the alcohols are easily converted into oxidation products, and nitric acid readily parts with oxygen, and is reduced to nitrous acid, so that by heating the main products of the reaction are aldehydes, organic acids, and nitrites of the alcohol radicals. In order to prevent the formation of these, the reaction must be so managed either that the oxidising action of the nitric acid cannot occur, or that the nitrous acid shall be destroyed before it can act on the alcohols.

1. The first problem may be accomplished by mixing the alcohol and acid in a platinum basin cooled by a freezing mixture to −18° to −20°, both alcohol and acid having been previously cooled to considerably below 0°.

2. In order to destroy any nitrous acid that may be formed, urea is added to the acid before addition of the alcohol; as previously mentioned (§ 136), this reduces nitrous acid very readily according to the equation :

$$CO.(NH_2)_2 + 2HNO_2 = CO_2 + 3H_2O + 2N_2.$$

If the nitric acid was pretty free from trioxide or tetroxide of nitrogen at starting, a relatively small quantity of urea completely answers this purpose.

The nitrates of the alcohol radicals decompose on heating to high temperatures, mostly with explosion, consequent on the partial oxidation of the carbo-hydrogen radical by the oxygen of the acid group. They are easily saponified by heating with alkalies :

$$C_nH_{2n+1}.O.NO_2 + KOH = KO.NO_2 + C_nH_{2n+1}.OH.$$

212. The following are the best known :—

Methylic nitrate, $CH_3.ONO_2$, is a colourless, heavy liquid, little soluble in water, which boils at 66° and whose vapour detonates at 150°.

Ethylic nitrate, $C_2H_5O.NO_2$, is obtained by distillation of 60 grams of alcohol with the same weight of nitric acid of sp. gr. 1·4, one gram of urea being also added. It is not advisable to prepare larger quantities, on account of the danger of an explosion. At first aqueous alcohol distils over, later the ethylic nitrate. It is a colourless, agreeable-smelling liquid, of sp. gr. 1·112 at 17°, which boils at 85°, and whose vapour on over-heating decomposes with explosion. It is nearly insoluble in water.

Isobutylic nitrate, $(CH_3)_2CH.CH_2.O.NO_2$, is obtained by action of argentic nitrate on isobutylic iodide, as a liquid boiling at 123° and of sp. gr. 1·038 at 0° :

$$C_4H_9I + Ag.O.NO_2 = AgI + C_4H_9.O.NO_2.$$

Isoamylic nitrate, $(CH_3)_2CH.CH_2.CH_2.O.NO_2$, is a colourless oil, boiling at 148°, which, from 7° to 8°, has the sp. gr. 1·000; at lower temperatures is heavier, at higher temperatures lighter, than water of like temperature.

Nitrites of the Alcohol Radicals, $C_nH_{2n+1}.O.NO$.

213. The true nitrites of the alcohol radicals are prepared in the impure condition by the action of nitric acid upon the alcohols (§ 211); in greater purity by passing the vapour of nitrous anhydride into the cooled alcohol:

$$2C_nH_{2n+1}.OH + N_2O_3 = 2C_nH_{2n+1}.O.NO + H_2O,$$

or by distillation of the alcohol with potassic nitrite and sulphuric acid.

They are more readily volatile than the corresponding nitrates, and are in part employed in medicine. Mixed with potassic hydrate, they yield alcohol and potassic nitrite. After a time, especially if exposed to light, they spontaneously decompose with formation of oxidation products of the alcohol radical and nitrogen gas.

The nitro-ethanes, $C_nH_{2n+1}.NO_2$ (§ 289), are isomeric with these bodies.

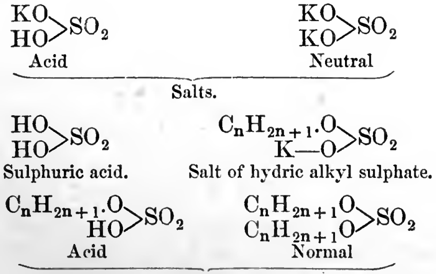
Methylic nitrite, $CH_3.O.NO$, is, at ordinary temperatures, a mobile gas of agreeable odour, condensable by cold to a colourless liquid, which boils at −12°.

Ethylic nitrite, $C_2H_5.O.NO$, boils at +16°, and has below this temperature sp. gr. ·947. It is insoluble in water. 'Sweet spirits of nitre' is a mixture of ethylic nitrite with ethylic alcohol and oxidation products of the latter, especially aldehyde and ethylic acetate. In order to prepare it eight parts of strong alcohol are mixed with one part of fuming nitric acid, and, after standing twenty-four hours, distilled; the distillate is shaken with potassic carbonate in order to remove any free acid, and then again rectified.

Isoamylic nitrite, $(CH_3)_2CH.CH_2.CH_2.O.NO$, is a liquid boiling at 96°, whose vapour, when inhaled, produces violent headache.

Alkylic Sulphates.

214. As sulphuric acid forms with monovalent metals acid and neutral salts, so similarly it yields with the alcohol radicals acid and neutral sulphates. The acid sulphates behave as monobasic acids, exchanging the hydroxylic hydrogen for metals, and so forming neutral salts:



$$\underbrace{\underset{\text{Acid}}{\left.\begin{matrix}KO\\HO\end{matrix}\right>SO_2}\qquad\qquad\underset{\text{Neutral}}{\left.\begin{matrix}KO\\KO\end{matrix}\right>SO_2}}_{\text{Salts.}}$$

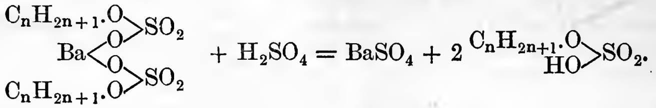
$$\underset{\text{Sulphuric acid.}}{\left.\begin{matrix}HO\\HO\end{matrix}\right>SO_2}\qquad\qquad\underset{\text{Salt of hydric alkyl sulphate.}}{\left.\begin{matrix}C_nH_{2n+1}.O\\K—O\end{matrix}\right>SO_2}$$

$$\underbrace{\underset{\text{Acid}}{\left.\begin{matrix}C_nH_{2n+1}.O\\HO\end{matrix}\right>SO_2}\qquad\qquad\underset{\text{Normal}}{\left.\begin{matrix}C_nH_{2n+1}O\\C_nH_{2n+1}O\end{matrix}\right>SO_2}}_{\text{Alkylic sulphate.}}$$

215. *The Acid Alkylic Sulphates.*—On mixing an alcohol with concentrated sulphuric acid, the acid sulphate is formed with very considerable evolution of heat, though the ingredients only react partially on one another (§ 201). To obtain the product, the cooled and diluted mixture is neutralised with the carbonate of one of those metals which yield insoluble sulphates—barium, strontium, or lead. In this way the sulphuric acid, remaining unchanged according to the equation:

$$xC_nH_{2n+1}.OH + yH_2SO_4 = zC_nH_{2n+1}.HSO_4 + zH_2O \\ + (x-z)C_nH_{2n+1}.OH + (y-z)H_2SO_4,$$

is removed from the solution, whilst the alkylic metallic sulphate remains dissolved. This can be purified by recrystallisation, and from its solution, by precipitation of the metal, an aqueous solution of the acid alkylic sulphate obtained:



$$Ba\left<\begin{matrix}O\\O\end{matrix}\right. \begin{matrix}\begin{matrix}C_nH_{2n+1}.O\\ O\end{matrix}\!>SO_2\\ \begin{matrix}O\\ C_nH_{2n+1}.O\end{matrix}\!>SO_2\end{matrix} + H_2SO_4 = BaSO_4 + 2\begin{matrix}C_nH_{2n+1}.O\\HO\end{matrix}\!>SO_2.$$

By evaporation in vacuo at ordinary temperatures the solution can be concentrated, and the acid sulphates obtained generally as strongly acid syrupy liquids.

By long standing in aqueous solution the reciprocal process to that of their formation, decomposition into alcohol and free acid, slowly ensues; on boiling this results in shorter time, and the alcohol distils over:

$$C_nH_{2n+1}.HSO_4 + H_2O + xH_2O = C_nH_{2n+1}.OH + H_2SO_4 + xH_2.$$

This is a reaction exactly analogous to that already given (§ 201) as that of an alcohol at high temperature:

$$C_nH_{2n+1}.HSO_4 + C_mH_{2m+1}.OH = C_nH_{2n+1}.O.C_mH_{2m+1} + H_2SO_4.$$

On heating the pure acid sulphates by themselves, sulphuric acid is regenerated, and by removal of hydrogen an olefine formed:

$$C_nH_{2n+1}.H.SO_4 = H_2SO_4 + C_nH_{2n}.$$

The metallic salts of these bodies behave similarly. On boiling with water they decompose slowly into acid metallic sulphates and alcohol:

$$C_nH_{2n+1}.M.SO_4 + H_2O + xH_2O = HMSO_4 + C_nH_{2n+1}.OH \\ + xH_2O;$$

and this decomposition occurs especially readily if the solution contains free acid. It is therefore necessary in evaporating solutions of these salts to have a little carbonate or metallic hydrate present. A larger quantity of the latter in concentrated solution, on the other hand, completely decomposes the compound:

$$C_nH_{2n+1}.KSO_4 + KOH = K_2SO_4 + C_nH_{2n+1}.OH.$$

By dry distillation the metallic alkylic sulphates yield chiefly acid metallic salts and olefines:

$$C_nH_{2n+1}.KSO_4 = HKSO_4 + C_nH_{2n},$$

other processes, however, occurring, such as polymerisation of the olefine molecule and formation of further sulphuric acid derivatives of, at present, not clearly explained nature.

From the olefines the acid alkylic sulphates can be obtained by direct union with sulphuric acid. These hydrocarbons are absorbed by concentrated sulphuric acid:

$$C_nH_{2n} + xH_2SO_4 = C_nH_{2n+1}.HSO_4 + (x-1)H_2SO_4,$$

and from this mixture the pure body obtained by conversion into the barium salt, &c., as already described. Except in the case of ethylene, the acid salts obtained are not those of the primary but of secondary or tertiary alcohol radicals (compare § 163).

216. Of these compounds the following may be mentioned:—

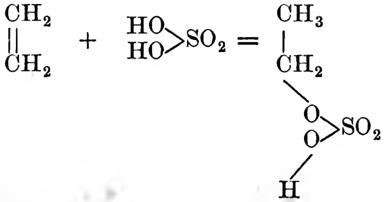
Hydric methylic sulphate, or *methyl-sulphuric acid*, $CH_3.H.SO_4$, is formed by mixing two parts of concentrated sulphuric acid with one part of methylic alcohol. By neutralisation with baric carbonate, and evaporation of the liquid filtered from the baric sulphate, *baric methylic sulphate* is obtained:

$$Ba(O.SO_2.O.CH_3)_2,2H_2O.$$

By dissolving this salt in water, precipitating the barium by the requisite amount of sulphuric acid, and evaporating the liquid in vacuo, hydric methylic sulphate is obtained in white, strongly acid needles, very readily soluble in water, less easily in absolute alcohol. By saturation with metallic oxides or carbonates the metallic methylic sulphates can be obtained, which are, without exception, soluble in water.

Hydric ethylic sulphate, or *ethyl-sulphuric acid*, $C_2H_5.HSO_4$, is obtained by mixing equal parts of strong sulphuric acid and ethylic alcohol, and treatment similar to the last, as a clear syrupy liquid of sp. gr. 1·317. The *potassic* salt, $C_2H_5.K.SO_4$, crystallises in colourless tables, very soluble in water, as is also *calcic ethyl sulphate*, $(C_2H_5)_2Ca(SO_4)_2,2H_2O$, which loses its water of crystallisation in vacuo over sulphuric acid.

Hydric ethylic sulphate is also formed by bringing together ethylene (olefiant gas) and sulphuric acid:



This compound can therefore be obtained from ordinary coal gas, which contains ethylene, and by its means ethylic alcohol also prepared.

Hydric isoamylic sulphate, isoamyl sulphuric acid, $C_5H_{11}.HSO_4$. By mixing fermentation amylic alcohol with its own weight of concentrated sulphuric acid, dilution with water, neutralisation by baric carbonate, and evaporation of the filtrate, two isomeric baric amylsulphates are obtained, crystallising in large leaves, and which, on account of their different solubility in water, can be separated from one another by repeated crystallisation.

The more readily soluble barium salt is that of the optically active;

the less soluble, which occurs in larger quantity, that of the inactive amylic alcohol. From them the respective modifications of the alcohols can be prepared by distillation with water (§ 170, 4 and 7).

The Neutral Alkylic Sulphates.

217. The only neutral sulphate that can be prepared in the pure state by heating the alcohol with sulphuric acid is

Dimethylic sulphate, $(CH_3)_2SO_4$:

$$2CH_3.OH + H_2SO_4 = (CH_3)_2SO_4 + H_2O.$$

For this purpose one part of methylic alcohol is distilled with eight to ten parts of strong sulphuric acid, and the portion distilling at 150° collected separately. This is then washed with water, the oil remaining undissolved, dried by calcic chloride and repeatedly rectified. The boiling point of the pure sulphate is 188°, the sp. gr. = 1·234. It has a garlic odour, is not soluble in water, but is slowly decomposed by it into methylic alcohol and hydric methylic sulphate:

$$(CH_3)_2SO_4 + H_2O = CH_3.OH + CH_3.H.SO_4.$$

Distilled with sodic chloride, it yields methylic chloride:

$$(CH_3)_2SO_4 + 2NaCl = 2CH_3.Cl + Na_2SO_4.$$

Diethylic sulphate is formed by the action of sulphuric anhydride upon ethylic alcohol or ether, together with isethionic acid and isethionic anhydride. It is generally prepared by passing the vapour of sulphuric anhydride into anhydrous ether, cooled by a freezing mixture:

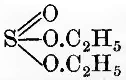
$$(C_2H_5)_2O + SO_3 = (C_2H_5)_2SO_4.$$

The resultant syrupy liquid is diluted with water, and shaken with ethylic ether, by which the sulphate is dissolved. The ethereal layer is then separated from the lower aqueous acid solution, and evaporated in vacuo. Diethylic sulphate remains as an oily liquid of peppermint odour, sp. gr. 1·12. By heating it decomposes with formation of ethylene, and therefore cannot be obtained by distillation. Heated with water it yields ethylic alcohol and the acid sulphate.

Sulphites of the Alcohol Radicals.

218. Of the alkylic salts of sulphurous acid, $SO(OH)_2$, only the normal salts are known. They are prepared by action of thionyl dichloride on the alcohols:

$$SOCl_2 + 2C_2H_5.OH = 2HCl + (C_2H_5.O)_2SO,$$

or 

$$S\begin{cases}=O\\ -O.C_2H_5\\ -O.C_2H_5\end{cases}$$

together with the alkylic chlorides. They are formed in more complicated reaction by mixing alcohols with chloride of sulphur, together with sulpho-alcohols (mercaptans), alcoholic chlorides, separation of sulphur, hydrochloric acid, &c.; e.g.

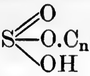
$$S_2Cl_2 + 3C_2H_5.OH = SO(OC_2H_5)_2 + \underset{\text{(Mercaptan.)}}{C_2H_5.SH} + 2HCl.$$

They are separated from the mixed products by fractional distillation.

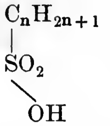
Ethylic sulphite of the above-given formula is a liquid boiling at 160°, of 1·085 sp. gr. at 16°, and of peculiar peppermint-like odour. It is insoluble in water, but is slowly decomposed thereby into ethylic alcohol and sulphurous anhydride:

$$(C_2H_5)_2SO_3 + H_2O = 2C_2H_5.OH + SO_2.$$

By dry chlorine gas, with exposure to sun-light, it is decomposed, yielding perchlor-ethane, (C_2Cl_6), trichlor-acetyl chloride, ($CCl_3.COCl$), and sulphuryl chloride, SO_2Cl_2:



The acid alkylic sulphites, $S\begin{cases} O \\ O.C_nH_{2n+1} \\ OH \end{cases}$, have not yet been obtained, but the bodies isomeric with them, the alkyl sulphonic acids:

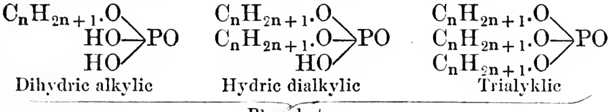


$$\begin{array}{l} C_nH_{2n+1} \\ | \\ SO_2 \\ \quad \diagdown \\ \quad OH \end{array}$$

are known, and will be described amongst the compounds of the alcohol radicals with sulphur.

Compounds of the Alcohol Radicals with the Phosphorus Acids.

219. Tribasic orthophosphoric acid can yield three different alkylic salts, corresponding to its metallic compounds:



$$\left.\begin{array}{r} C_nH_{2n+1}.O \\ HO \\ HO \end{array}\right\rangle PO \qquad \left.\begin{array}{r} C_nH_{2n+1}.O \\ C_nH_{2n+1}.O \\ HO \end{array}\right\rangle PO \qquad \left.\begin{array}{r} C_nH_{2n+1}.O \\ C_nH_{2n+1}.O \\ C_nH_{2n+1}.O \end{array}\right\rangle PO$$

Dihydric alkylic — Hydric dialkylic — Trialyklic

Phosphates.

of which the two hydric salts behave as a dibasic and monobasic acid respectively.

It will suffice in this place to describe the ethylic compounds. The others are either not prepared, or are so similar in properties and preparation as to make a description superfluous.

If syrupy orthophosphoric acid be mixed with absolute alcohol, there results mono-ethylic phosphate, together with a little diethylic phosphate, certain quantities of the phosphoric acid and alcohol also remaining unchanged:

$$aH_3PO_4 + bC_2H_5.OH = xC_2H_5.H_2.PO_4 + y(C_2H_5)_2HPO_4$$
$$+ (a-x-y)H_3PO_4 + (b-x-2y)C_2H_5.OH + (x + 2y)H_2O.$$

A better yield of both compounds is obtained by long standing of alcohol and glacial metaphosphoric acid under a bell jar; the vapour of the first is slowly absorbed, with formation of dihydric ethylic phosphate:

$$HPO_3 + C_2H_5.OH = (C_2H_5)H_2PO_4,$$

which by further action of the alcohol is partly converted into diethylic phosphate:

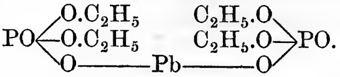
$$(C_2H_5)H_2PO_4 + C_2H_5.OH = (C_2H_5)_2HPO_4 + H_2O;$$

the water so formed converting unchanged metaphosphoric into the tribasic acid, which, acting on the alcohol, gives small amounts of both salts.

A still better yield is obtained by allowing phosphoric anhydride to deliquesce in alcohol vapour:

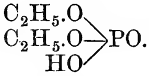
$$P_2O_5 + 3C_2H_5.OH = C_2H_5.H_2.PO_4 + (C_2H_5)_2HPO_4.$$

In every case the crude product is diluted with water and neutralised by plumbic carbonate; plumbic phosphate, $Pb_3(PO_4)_2$, and plumbic ethylic phosphate, $C_2H_5.Pb.PO_4$, separate, being insoluble, and the clear filtrate contains only plumbic diethylic phosphate:



$$PO\left\langle\begin{array}{l}O.C_2H_5\\O.C_2H_5\\O\text{———}Pb\text{———}O\end{array}\right.\begin{array}{r}C_2H_5.O\\C_2H_5.O\\\end{array}\Big\rangle PO.$$

By evaporation of the solution this latter separates in silky needles which melt at 180°. If their solution be decomposed by hydric sulphate, and the plumbic sulphide filtered off, the solution contains *Diethylic phosphate,*



$$\left.\begin{array}{r}C_2H_5.O\\C_2H_5.O\\HO\end{array}\right\rangle PO.$$

By evaporation in a vacuum it remains as a strongly acid syrup, which yields in most cases readily soluble and crystallisable salts with metallic oxides or carbonates.

The lead salt of monethylic phosphate, being insoluble, is found in the residue. If this be suspended in water, and hydric sulphide passed through the liquid, phosphoric acid and monethylic phosphate go into solution; after filtration the liquid is more than neutralised with baric carbonate, and the insoluble baric phosphate filtered off. On evaporation of the filtrate *baric ethylic phosphate*, $C_2H_5.Ba.PO_4,6H_2O$, crystallises in colourless six-sided prisms, from which, by addition of the requisite quantity of sulphuric acid, *monethylic phosphate* is set free, and can be obtained by evaporation of the filtered liquid as a strongly acid syrup. On heating, alcohol, ethylic ether, and later ethylene, are evolved, and a residue of metaphosphoric acid and carbon is left.

Triethylic phosphate, $(C_2H_5)_3PO_4$, is formed, together with a salt of monethylic phosphate, by the dry distillation of a salt of diethylic phosphate; e.g.

$$Pb(C_2H_5)_4P_2O_8 = (C_2H_5)_3PO_4 + Pb.(C_2H_5)PO_4\,;$$

also by action of phosphoric anhydride on pure ethylic ether:

$$P_2O_5 + 3(C_2H_5)_2O = 2(C_2H_5)_3PO_4\,;$$

and by addition of phosphoric oxychloride to an alcoholic solution of sodic ethylate:

$$POCl_3 + 3NaOC_2H_5 = 3NaCl + PO(C_2H_5.O)_3.$$

Triethylic phosphate is a colourless neutral liquid, boiling at 215°, soluble in water, alcohol, and ether, and after a short time decomposed by the first into alcohol and diethylic phosphate.

220. Of the salts of the other modifications of phosphoric acid the best known is

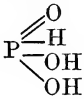
Tetra-ethylic pyrophosphate, $(C_2H_5)_4P_2O_7$. It is obtained by heating argentic pyrophosphate with ethylic iodide in closed tubes at 100° :

$$Ag_4P_2O_7 + 4C_2H_5I = 4AgI + (C_2H_5)_4P_2O_7.$$

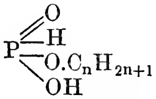
It is separated from the argentic iodide by solution in ethylic ether, and on evaporation of that solvent remains as a viscous liquid, is easily soluble in water, and reacts with it, probably according to the equation :

$$(C_2H_5)_4P_2O_7 + H_2O = 2(C_2H_5)_2HPO_4.$$

221. The alkylic phosphites are obtained from phosphorous trichloride, which, when heated with alcohol containing a little water, yields hydrochloric acid, alkylic chlorides, and mon-alkylic phosphites, which by evaporation are obtained as acid syrups, and contain only *one* atom of replaceable hydrogen. If ordinary phosphorous acid be expressed by the formula :

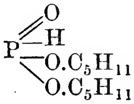


these acid salts would be :



The methylic, ethylic, and amylic metallic salts are mostly extremely soluble and difficultly crystallisable.

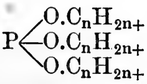
By action of anhydrous alcohols upon phosphorous trichloride *dialkylic phosphites* are formed; at least an isoamylic salt is so prepared :

$$PCl_3 + 3(HO.C_5H_{11}) = 2HCl + C_5H_{11}Cl +$$ 

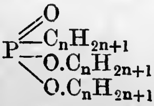
At the same time trialkylic phosphites, $(C_nH_{2n+1})_3PO_3$, are formed, which, however, are better obtained by action of phosphorous trichloride on sodic alkylates :

$$PCl_3 + 3NaOC_nH_{2n+1} = 3NaCl + PO_3(C_nH_{2n+1})_3.$$

These unpleasant-smelling bodies are derived from a phosphorous acid, $P(OH)_3$, and must be expressed :

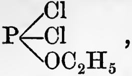


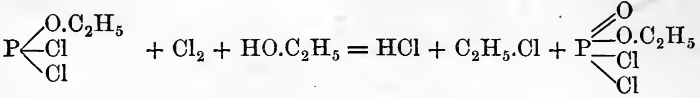
as on saponification they are completely decomposed into alcohol and a metallic phosphite, and on oxidation by nitric acid are converted into phosphoric acid ; whilst if of the formula



on saponification they would yield the salt of a monalkylic phosphoric acid (§ 304), and on oxidation the acid itself.

Triethylic phosphite, $P(O.C_2H_5)_3$, boils at 191°, and has sp. gr. 1·075. It mixes readily with alcohol and water.

222. If in the action of PCl_3 on alcohol the former be in excess, it yields, as well as the previous bodies, *ethylic phosphite dichloride*,  $P\left\langle\begin{matrix}Cl\\Cl\\OC_2H_5\end{matrix}\right.$, as a colourless liquid of 1·316 sp. gr. and boiling at 117°. By passing chlorine through an alcoholic solution of this liquid, *ethylic phosphate dichloride*, boiling at 167°, is produced, according to the equation :



$$P\left\langle\begin{matrix}O.C_2H_5\\Cl\\Cl\end{matrix}\right. + Cl_2 + HO.C_2H_5 = HCl + C_2H_5.Cl + P\left\langle\begin{matrix}=O\\O.C_2H_5\\Cl\\Cl\end{matrix}\right.$$

223. Arsenic and arsenious acids yield compounds which generally correspond to those of the phosphorous acids. The normal salts are most readily prepared by action of alkylic iodides upon the argentic salts ; e.g.

$$AsO(OAg)_3 + 3IC_2H_5 = 3AgI + AsO(C_2H_5O)_3.$$

Triethylic arseniate can be distilled unchanged under reduced pressure.

The normal arsenites are best prepared from arsenious tribromides and the sodic alkylate. *Trimethylic arsenite*, $As(O.CH_3)_3$, boils at 120° ; *triethylic arsenite*, $As(OC_2H_5)_3$, at 166°–168°. Both are at once decomposed by water :

$$2As(O.C_2H_5)_3 + 3H_2O = As_2O_3 + 6C_2H_5.OH$$

Alkylic Borates.

224. The ortho-borates, corresponding to $B(OH)_3$, are obtained without difficulty by passing boron trichloride into the alcohols, or by heating the latter with boric anhydride. At the same time the salts of metaboric acid, BO.OH, are invariably formed. On distilling the mixture the trialkylic borates and unchanged alcohols pass over, whilst the metaborate remains behind. Also by heating crystallised boric acid with alcohol small quantities of these compounds are formed, which, evaporating with the alcohol, impart their characteristic green coloration to its flame.

The alkylic ortho-borates are colourless liquids.

Trimethylic borate, $B(O.CH_3)_3$, boils at 65°.

Triethylic borate, $B(O.C_2H_5)_3$, boils at 120°, and has sp. gr. ·887.

Tri-isoamylic borate, $B(O.C_5H_{11})_3$, boils at 255°.

On heating these with boric anhydride they yield metaborates :

$$B(O.C_nH_{2n+1})_3 + B_2O_3 = 3BO(O.C_nH_{2n+1}),$$

which are all syrupy liquids. On distillation they split up into the volatile ortho-borates, and a residue, glacial on cooling, of a salt of monobasic triboric acid :

$$4BO(O.C_nH_{2n+1}) = B(O.C_nH_{2n+1})_3 + B_3O_4(O.C_nH_{2n+1}).$$

All alkylic salts of boric acid are decomposed by water into boric acid and alcohol; those of the tribasic acid become turbid on exposure to moist air.

Alkylic Silicates.

225. The alkylic silicates are formed by action of silicic tetrachloride on the alcohols:

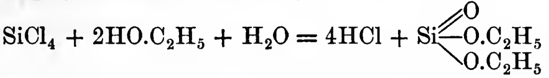
$$SiCl_4 + 4(HO.C_nH_{2n+1}) = 4HCl + Si(O.C_nH_{2n+1})_4.$$

The known compounds are distillable liquids, insoluble in water, by which they are slowly decomposed into alcohols and glacial hydrated silica. This latter is so hard that it scratches glass, and is very similar to the mineral hydrophane.

Ethylic silicate, $Si(OC_2H_5)_4$, is a colourless, mobile liquid of sp. gr. ·933 at 20°, boiling at 165°.

Isoamylic silicate, $Si(O.C_5H_{11})_4$, boils at 320°–325°, and has sp. gr. ·868.

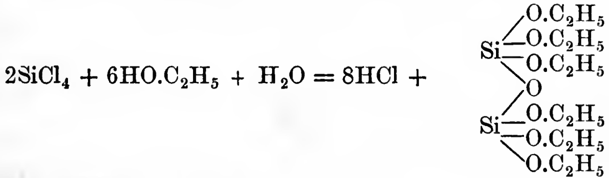
At the same time as the ortho-silicates others are formed, such as those derived from metasilicic acid, which are alone formed when the alcohols employed contain water; e.g.



$$SiCl_4 + 2HO.C_2H_5 + H_2O = 4HCl + Si\left\{\begin{array}{l}O\\O.C_2H_5\\O.C_2H_5\end{array}\right.$$

Diethylic silicate of this formula is a colourless thick liquid, which boils at 350°, and is decomposed into alcohol and amorphous acid by water.

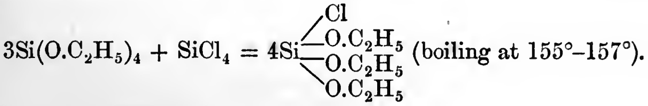
Compounds of the polysilicic acids are known; they are formed in presence of only very little water, according to the equation:



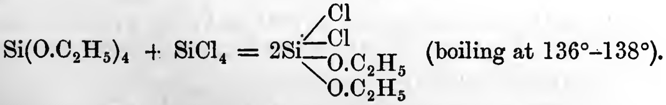
$$2SiCl_4 + 6HO.C_2H_5 + H_2O = 8HCl + \begin{array}{l}Si\left\{\begin{array}{l}O.C_2H_5\\O.C_2H_5\\O.C_2H_5\end{array}\right.\\ \quad O\\ Si\left\{\begin{array}{l}O.C_2H_5\\O.C_2H_5\\O.C_2H_5\end{array}\right.\end{array}$$

hexethylic disilicate, boiling at 230°–240°.

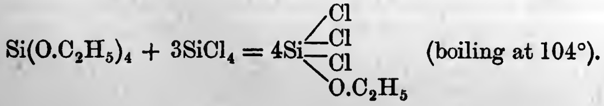
226. If ethylic orthosilicate be heated with silicic chloride in sealed tubes, they unite to form chlor silicates:



$$3Si(O.C_2H_5)_4 + SiCl_4 = 4Si\left\{\begin{array}{l}Cl\\O.C_2H_5\\O.C_2H_5\\O.C_2H_5\end{array}\right. \text{(boiling at 155°–157°).}$$



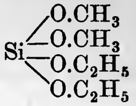
$$Si(O.C_2H_5)_4 + SiCl_4 = 2Si\left\{\begin{array}{l}Cl\\Cl\\O.C_2H_5\\O.C_2H_5\end{array}\right. \text{(boiling at 136°–138°).}$$



$$Si(O.C_2H_5)_4 + 3SiCl_4 = 4Si\left\{\begin{array}{l}Cl\\Cl\\Cl\\O.C_2H_5\end{array}\right. \text{(boiling at 104°).}$$

These chlor silicates, on treatment with ethylic alcohol, again yield ethylic orthosilicate; with other alcohols, mixed salts; e.g.

$$Si\begin{cases}Cl_2\\(O.C_2H_5)_2\end{cases} + 2HO.CH_3 = 2HCl +$$



Dimethylic diethylic silicate. Boils at 143°–147°.

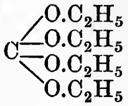
&c.

Alkylic Carbonates.

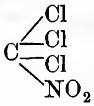
227. The number of alkylic salts derivable from carbonic acid is considerably greater than that of the metallic salts. In the latter it acts only as a dibasic acid, but with the alcohol radicals also as a tetrabasic acid. It has, therefore, considerable analogy with silicic acid.

For instance, by action of sodic ethylate upon chlorpicrin

Tetra-ethylic carbonate, or *ethylic ortho-carbonate*,



is formed, according to the equation :



$$+ 4NaO.C_2H_5 = 3NaCl + NaNO_2 + C(O.C_2H_5)_4,$$

as a liquid boiling at 158°–159°, and converted by aqueous alkalies into alcohol and a metallic carbonate :

$$C.(OC_2H_5)_4 + 2KOH + H_2O = K_2CO_3 + 4(HO.C_2H_5).$$

228. The dialkylic carbonates, $CO.(O.C_nH_{2n+1})_2$, are prepared by the action of argentic carbonate upon the alkylic iodides :

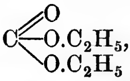
$$CO(OAg)_2 + 2C_nH_{2n+1}I = 2AgI + CO(O.C_nH_{2n+1})_2;$$

by heating the alkylic oxalates with sodium, to some extent by passing carbonic oxychloride into the alcohols :

$$COCl_2 + 2HO.C_nH_{2n+1} = 2HCl + CO(O.C_nH_{2n+1})_2;$$

and by action of bromine upon the alkylic ortho-carbonates.

Diethylic carbonate,

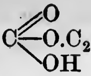


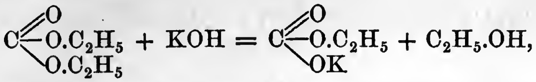
, a colourless liquid, of aromatic odour, insoluble in water, boiling at 126°, and of sp. gr. ·978 at 20°.

Dipropylic carbonate, $CO.(O.CH_2.CH_2.CH_3)_2$, a colourless mobile liquid, boils at 160°–165°.

Diisobutylic carbonate, $CO\left(O.CH_2.CH<\begin{matrix}CH_3\\CH_3\end{matrix}\right)_2$, a pleasant-smelling liquid, boiling at 190°.

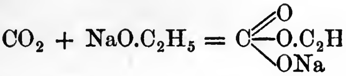
Diisoamylic carbonate, $CO.(O.C_5H_{11})_2$, boils at 225°, and has sp. gr. ·9144.

229. Acids salts of the formula  $\mathrm{C}\left\langle\begin{array}{l}\mathrm{O}\\\mathrm{O.C_2H_5}\\\mathrm{OH}\end{array}\right.$ are not known, but their metallic salts are; they are formed by adding to the normal alkylic carbonates a quantity of basic hydrate insufficient for their complete saponification:



$$\mathrm{C}\left\langle\begin{array}{l}\mathrm{O}\\\mathrm{O.C_2H_5}\\\mathrm{O.C_2H_5}\end{array}\right. + \mathrm{KOH} = \mathrm{C}\left\langle\begin{array}{l}\mathrm{O}\\\mathrm{O.C_2H_5}\\\mathrm{OK}\end{array}\right. + \mathrm{C_2H_5.OH},$$

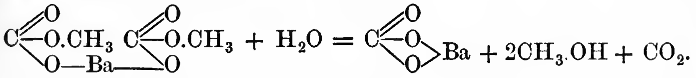
and by passing carbonic anhydride through alcoholic solutions of the metallic alkylates:



$$\mathrm{CO_2} + \mathrm{NaO.C_2H_5} = \mathrm{C}\left\langle\begin{array}{l}\mathrm{O}\\\mathrm{O.C_2H}\\\mathrm{ONa}\end{array}\right.$$

Solutions of the alkalies and of baric hydrate in absolute alcohol always contain some quantities of the respective metallic alkylates (§ 198); on addition of dry carbonic anhydride, therefore, there is formed, in addition to a precipitate of metallic carbonate, also a metallic alkylic carbonate, which being somewhat soluble in alcohol, can be separated from the metallic carbonate and obtained in the crystalline condition by addition of ethylic ether to the solution.

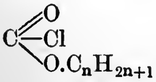
The metallic alkylic carbonates mostly form scaly crystals of silky lustre, which are soluble in water, and are decomposed thereby, most quickly on heating:

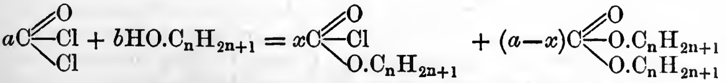


$$\mathrm{C}\left\langle\begin{array}{l}\mathrm{O}\\\mathrm{O.CH_3}\\\mathrm{O{-}Ba{-}}\end{array}\right.\mathrm{C}\left\langle\begin{array}{l}\mathrm{O}\\\mathrm{O.CH_3}\\\mathrm{O}\end{array}\right. + \mathrm{H_2O} = \mathrm{C}\left\langle\begin{array}{l}\mathrm{O}\\\mathrm{O}\\\mathrm{O}\end{array}\right\rangle\mathrm{Ba} + \mathrm{2CH_3.OH} + \mathrm{CO_2}.$$

By dry distillation with metallic alkylic sulphates, or by heating with alkylic iodides, they are converted into normal salts; this method can be used for preparing the so-called 'mixed salts,' i.e. those containing two different alcohol radicals:

$$\mathrm{K(C_2H_5)CO_3} + \mathrm{K(CH_3)SO_4} = \mathrm{(CH_3)(C_2H_5)CO_3} + \mathrm{K_2SO_4}.$$

230. The chief products of the action of carbonic oxychloride upon alcohols are not normal carbonates, but the *alkylic chloro-carbonates*,  $\mathrm{C}\left\langle\begin{array}{l}\mathrm{O}\\\mathrm{Cl}\\\mathrm{O.C_nH_{2n+1}}\end{array}\right.$, so that the reaction corresponds more to the equation:



$$a\mathrm{C}\left\langle\begin{array}{l}\mathrm{O}\\\mathrm{Cl}\\\mathrm{Cl}\end{array}\right. + b\mathrm{HO.C_nH_{2n+1}} = x\mathrm{C}\left\langle\begin{array}{l}\mathrm{O}\\\mathrm{Cl}\\\mathrm{O.C_nH_{2n+1}}\end{array}\right. + (a-x)\mathrm{C}\left\langle\begin{array}{l}\mathrm{O}\\\mathrm{O.C_nH_{2n+1}}\\\mathrm{O.C_nH_{2n+1}}\end{array}\right.$$

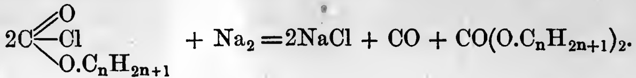
$$+ (2a-x)\mathrm{HCl} + (b-2a+x)\mathrm{HO.C_nH_{2n+1}},$$

where b must at least $= 2a$, and x is invariably larger than $\frac{1}{2}a$. The two products are separated by fractional distillation.

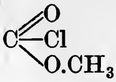
The *alkylic chloro-carbonates* are liquids insoluble in water and of unpleasant odour. By water they are soon decomposed:

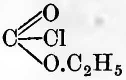
$$\mathrm{CO.Cl(O.C_nH_{2n+1})} + \mathrm{H_2O} = \mathrm{HCl} + \mathrm{HO.C_nH_{2n+1}} + \mathrm{CO_2}.$$

Treated with sodium, they yield sodic chloride, carbonic monoxide, and neutral alkylic carbonates :



$$2C\left\langle\begin{array}{l}O\\Cl\\O.C_nH_{2n+1}\end{array}\right. + Na_2 = 2NaCl + CO + CO(O.C_nH_{2n+1})_2.$$

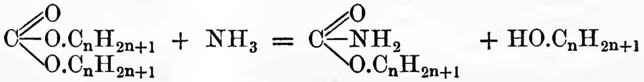
Methylic chloro-carbonate,  $C\left\langle\begin{array}{l}O\\Cl\\O.CH_3\end{array}\right.$, is a colourless mobile oil.

Ethylic chloro-carbonate,  $C\left\langle\begin{array}{l}O\\Cl\\O.C_2H_5\end{array}\right.$, is like the last, boils at 94°, and has sp. gr. 1·139 at 15°.

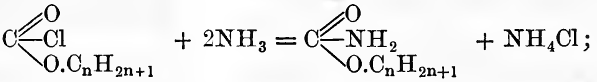
Propylic chloro-carbonate, $Cl.CO.O.CH_2.CH_2.CH_3$, boils between 120° and 130°.

Isobutylic chloro-carbonate, $Cl.CO.O.CH_2.CH\left\langle\begin{array}{l}CH_3\\CH_3\end{array}\right.$, decomposes by distillation.

231. *Alkylic carbamates,* also termed *urethanes,* are formed as the first decomposition products of alkylic normal carbonates and chloro-carbonates by ammonia :

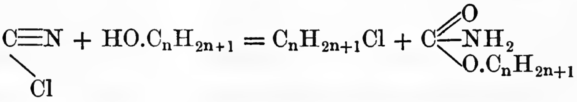


$$C\left\langle\begin{array}{l}O\\O.C_nH_{2n+1}\\O.C_nH_{2n+1}\end{array}\right. + NH_3 = C\left\langle\begin{array}{l}O\\NH_2\\O.C_nH_{2n+1}\end{array}\right. + HO.C_nH_{2n+1}$$



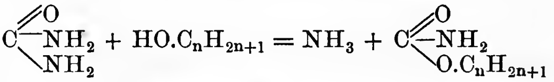
$$C\left\langle\begin{array}{l}O\\Cl\\O.C_nH_{2n+1}\end{array}\right. + 2NH_3 = C\left\langle\begin{array}{l}O\\NH_2\\O.C_nH_{2n+1}\end{array}\right. + NH_4Cl;$$

further by the action of cyanogen chloride on alcohols :



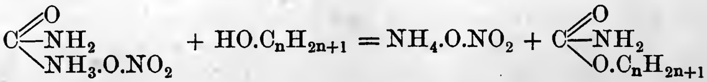
$$\begin{array}{l}C\equiv N\\ \diagdown\\ \quad Cl\end{array} + HO.C_nH_{2n+1} = C_nH_{2n+1}Cl + C\left\langle\begin{array}{l}O\\NH_2\\O.C_nH_{2n+1}\end{array}\right.$$

By heating urea with the alcohols to temperatures above 100°, they partly react on one another, forming carbamates :



$$C\left\langle\begin{array}{l}O\\NH_2\\NH_2\end{array}\right. + HO.C_nH_{2n+1} = NH_3 + C\left\langle\begin{array}{l}O\\NH_2\\O.C_nH_{2n+1}\end{array}\right.$$

This process can only be conducted with the higher boiling alcohols in open vessels, which allow the evolution of ammonia; for instance, with the amylic alcohols. By employing nitrate of urea instead of urea itself, the process can be applied to the lower boiling alcohols by employment of sealed tubes :

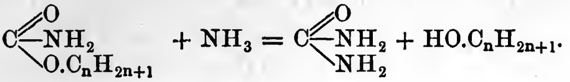


$$C\left\langle\begin{array}{l}O\\NH_2\\NH_3.O.NO_2\end{array}\right. + HO.C_nH_{2n+1} = NH_4.O.NO_2 + C\left\langle\begin{array}{l}O\\NH_2\\O.C_nH_{2n+1}\end{array}\right.$$

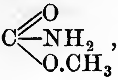
The alkylic carbamates are solid crystalline compounds, mostly readily soluble in alcohol and water. By strong bases they are converted into carbonates, ammonia, and alcohols :

$$C\left\{\begin{matrix}O\\NH_2\\O.C_nH_{2n+1}\end{matrix}\right. + 2KOH = CO(OK)_2 + NH_3 + HO.C_nH_{2n+1} ;$$

and by heating with excess of alcoholic ammonia, yield urea and alcohols :

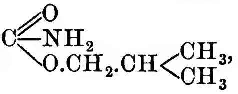


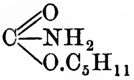
$$C\left\{\begin{matrix}O\\NH_2\\O.C_nH_{2n+1}\end{matrix}\right. + NH_3 = C\left\{\begin{matrix}O\\NH_2\\NH_2\end{matrix}\right. + HO.C_nH_{2n+1}.$$

Methylic carbamate,  $C\left\{\begin{matrix}O\\NH_2\\O.CH_3\end{matrix}\right.$, forms very hygroscopic tables, which melt at 55° and boil at 177°.

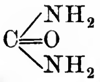
Ethylic carbamate, $CO.(NH_2)(O.C_2H_5)$, crystallises in glittering leaves, which melt below 100° and boil at about 180°.

Propylic carbamate, $CO(NH_2)(O.CH_2.CH_2.CH_3)$, large colourless prisms, which melt at 50° and are less soluble in water than in alcohol or ether.

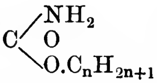
Isobutylic carbamate,  $C\left\{\begin{matrix}O\\NH_2\\O.CH_2.CH\!<\!\begin{matrix}CH_3\\CH_3\end{matrix}\end{matrix}\right.$, melts at 55° and boils at 207°.

Isoamylic carbamate,  $C\left\{\begin{matrix}O\\NH_2\\O.C_5H_{11}\end{matrix}\right.$, crystallises in easily soluble needles, melting at 66° and boiling at 220°.

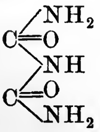
232. The *alkylic allophanates* stand in the same relation to biuret (§ 137) as the carbamates to urea :



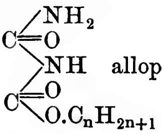
$C\left\{\begin{matrix}NH_2\\O\\NH_2\end{matrix}\right.$ urea.



$C\left\{\begin{matrix}NH_2\\O\\O.C_nH_{2n+1}\end{matrix}\right.$ carbamate.

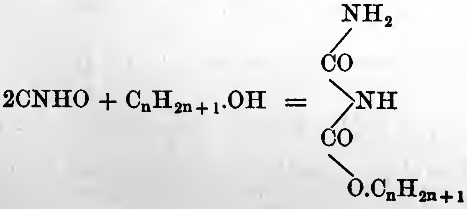


$\begin{matrix}C\left\{\begin{matrix}NH_2\\O\end{matrix}\right.\\>NH\\C\left\{\begin{matrix}O\\NH_2\end{matrix}\right.\end{matrix}$ biuret.



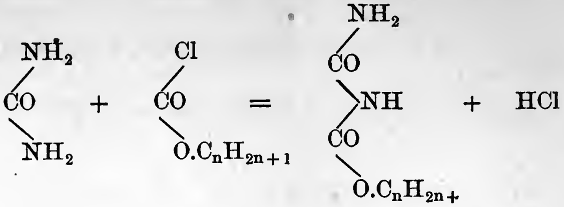
$\begin{matrix}C\left\{\begin{matrix}NH_2\\O\end{matrix}\right.\\>NH\\C\left\{\begin{matrix}O\\O.C_nH_{2n+1}\end{matrix}\right.\end{matrix}$ allophanate.

A general method of preparation consists in passing cyanic acid vapour into alcohols :

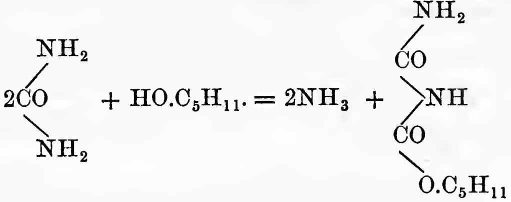


$$2CNHO + C_nH_{2n+1}.OH = \begin{matrix}NH_2\\CO\\>NH\\CO\\O.C_nH_{2n+1}\end{matrix}$$

They are easily obtained by heating alkylic chlor-carbonates with urea:



and also, together with carbamates, by the action of high-boiling alcohols upon urea at higher temperatures; e.g.



As they are more difficultly soluble in water than the carbamates formed at the same time (§ 231), they can be readily separated from the latter.

On submitting alkylic allophanates to dry distillation, they evolve alcohols, and leave a residue of cyanuric acid, which on further heating is resolved into cyanic acid:

$$3NH_2.CO.NH.CO.O.C_nH_{2n+1} = 3HO.C_nH_{2n+1} + 2C_3O_3N_3H_3.$$

On heating them in closed tubes at 100° with alcoholic ammonia, they yield biuret:

$$NH_2.CO.NH.CO.O.C_nH_{2n+1} + NH_3 = NH_2.CO.NH.CO.NH_2 + HO.C_nH_{2n+1}.$$

233. Methylic, ethylic, and isoamylic allophanates have been prepared; the two first crystallise in needles, the last in nacreous plates melting at 162°.

If the alkylic allophanates are rubbed together with baric hydrate in the cold, baric allophanate is formed, together with alcohol:

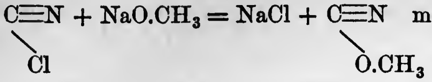
$$2(C_2H_5.O.CO.NH.CO.NH_2) + Ba(OH)_2 = Ba(O.CO.NH.CO.NH_2)_2 + 2C_2H_5.OH.$$

Baric allophanate, however, is very readily decomposed, and allophanic acid cannot be obtained by addition of strong acids, as it splits up into carbonic anhydride and urea:

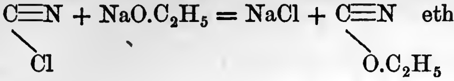
$$\left.\begin{array}{l}NH_2.CO.NH.CO.O\\NH_2.CO.NH.CO.O\end{array}\right>Ba + 2HCl = BaCl_2 + CO_2 + 2(NH_2.CO.NH_2).$$

Compounds of Alcohol Radicals with the Cyanogen Acids.

234. The true alkylic cyanates are very unstable liquids, insoluble in water, and are formed when the vapour of cyanogen chloride is passed into alcoholic solutions of metallic alkylate at a low temperature:

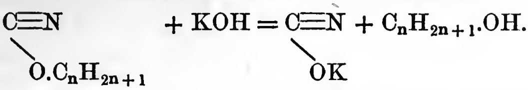


methylic cyanate.



ethylic cyanate.

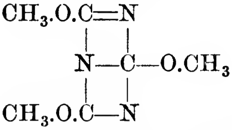
With alkalies they yield alcohol and a metallic cyanate:



The pseudocyanates are isomeric with the cyanates, and for a long time were mistaken for them. These, however, belong to the nitrogen compounds of the alcohol radicals, and will be considered later.

235. During their formation even, the alkylic cyanates partly polymerise, but completely on long standing, yielding thereby the solid, crystalline, alkylic true cyanurates. This change occurs especially easily with the methyl compound.

Methylic cyanurate, $C_3N_3(O.CH_3)_3$, or

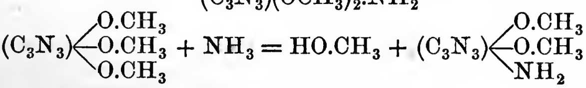


crystallises in colourless needles, easily soluble in ether, which melts at 134° and boils at 160°–170°. The distillate solidifies to a crystalline mass, which consists, however, of the isomeric *methylic pseudo-cyanurate*, which crystallises in thick prisms, melts at 175°, and will be further described amongst the nitrogen compounds of the alcohol radicals (§ 281).

Methylic cyanurate yields, on boiling with potassic hydrate, methylic alcohol and potassic cyanurate; by heating with ammonia it is converted into

Methylic ammelide, or *methylic amido-cyanurate:*

$$(C_3N_3)(OCH_3)_2.NH_2$$



$$(C_3N_3)\Big\langle\begin{matrix}O.CH_3\\O.CH_3\\O.CH_3\end{matrix} + NH_3 = HO.CH_3 + (C_3N_3)\Big\langle\begin{matrix}O.CH_3\\O.CH_3\\NH_2\end{matrix}$$

forming rhombic tables, melting at 212°, difficultly soluble in cold water and in ether, more readily in boiling water and in ethylic alcohol.

SULPHUR COMPOUNDS OF THE ALCOHOL RADICALS.

236. As far as is known the sulphides of the elements correspond to the oxides in their general chemical properties; this agreement of sulphur with oxygen also occurs in organic compounds, so that all organic sulphides containing dyad sulphur show very complete analogy to the oxygen compounds of corresponding composition.

The mercaptans, or thio-alcohols, $C_nH_{2n+1}.SH$, correspond to the alcohols; the thio-ethers, or alcoholic sulphides, $(C_nH_{2n+1})_2S$, to the ethers. In many cases the sulphur developes its higher valency, forming bodies without analogy among the mineral compounds of sulphur.

Mercaptans, or Thio-alcohols, $C_nH_{2n+1}.SH$.

237. The alkylic sulphhydrates, or thio-alcohols, can be prepared from many of the derivatives of the alcohol radicals already mentioned.

The alcohols are partly converted into the mercaptans when heated with phosphoric pentasulphide.. In a similar manner to its decomposition by water into phosphoric acid and hydric sulphide, it gives, in part, with alcohols, phosphoric acid and thio-alcohols.

The phosphoric acid is, at the same time, in considerable part converted into its alkylic salts, so that the main reaction may be represented by the equation :

$$P_2S_5 + 8(C_nH_{2n+1}.OH) = (C_nH_{2n+1})_2HPO_4 + (C_nH_{2n+1})H_2PO_4 + 5C_nH_{2n+1}.SH.$$

But as phosphoric pentasulphide behaves to the thio-alcohols similarly to P_2O_5 on the alcohols, alcoholic thio-phosphates are also formed.

From the haloid compounds of the alcohol radicals the mercaptans can be produced by heating with alcoholic solution of potassic sulphhydrate :

$$C_nH_{2n+1}Cl + KSH = C_nH_{2n+1}.SH + KCl.$$

A portion of the mercaptan first formed reacts on some still unchanged potassic sulphhydrate, forming the potassic thio-alkylate (compare § 197):

$$C_nH_{2n+1}.SH + KSH = SH_2 + C_nH_{2n+1}.S.K ;$$

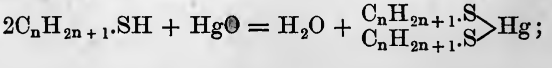
which in its turn reacting on the alkylic haloid compound, gives rise to the formation of thio-ethers :

$$C_nH_{2n+1}.SK + C_nH_{2n+1}Cl = (C_nH_{2n+1})_2S + KCl.$$

It is therefore generally preferable to submit a mixture of an alkylic potassic sulphate with potassic sulphhydrate to distillation :

$$(C_nH_{2n+1})KSO_4 + KSH = K_2SO_4 + C_nH_{2n+1}.SH.$$

238. The thio-alcohols are mostly liquids of most unpleasant garlic odour, which distil without decomposition and are nearly insoluble in water. Their sulphhydroxylic hydrogen atom is more easily replaced by metals than the hydroxylic hydrogen of alcohols, being not merely the case only by the alkalies, but also with equal or greater ease by those heavy metals which are precipitated from acid solutions by hydric sulphide. This reaction occurs with especial ease with mercury. On shaking an alcoholic solution of a thio-alcohol with mercuric oxide, a crystalline mercuric thio-alcoholate is formed, with considerable evolution of heat:



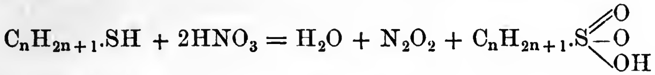
$$2C_nH_{2n+1}.SH + HgO = H_2O + \begin{matrix} C_nH_{2n+1}.S \\ C_nH_{2n+1}.S \end{matrix}\!\!>\!Hg ;$$

whilst with an alcoholic solution of mercuric chloride a precipitate of the difficultly soluble chlor-mercuric thio-alkylate is obtained :

$$C_nH_{2n+1}.SH + HgCl_2 = HCl + C_nH_{2n+1}.S—Hg—Cl.$$

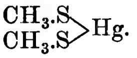
From these reactions the thio-alcohols have got the name mercaptans (from *mercurio-aptum*); the metallic derivatives are frequently termed mercaptides.

All oxidating bodies react very readily on the mercaptans, the more energetic, such as concentrated nitric acid, often with great violence. By such oxidation the sulphur is not separated from the carbon, but by taking up three atoms of oxygen is converted into the group $SO_2.OH$, which, united to the alcohol radical, forms a sulphonic acid :



$$C_nH_{2n+1}.SH + 2HNO_3 = H_2O + N_2O_2 + C_nH_{2n+1}.S\begin{cases}=O\\=O\\-OH\end{cases}$$

239. *Methylic mercaptan*, or *methylic thio-alcohol*, $CH_3.SH$, is a mobile liquid which floats on water, boils at 20°, and yields with mercuric oxide shining colourless plates of *mercuric sulph-methylate :*



$$\begin{matrix}CH_3.S\\CH_3.S\end{matrix}\!>\!Hg.$$

Ethylic mercaptan, or *ethylic thio-alcohol*, $C_2H_5.SH$, is a colourless mobile liquid, of sp. gr. ·835 and boiling at 36°. By quick evaporation in the air, e.g. a drop at the end of a glass rod, it absorbs heat so rapidly that a portion solidifies in crystalline leaves. *Mercuric ethylic mercaptide*, or *mercuric sulph-ethylate*, $\begin{matrix}C_2H_5.S\\C_2H_5.S\end{matrix}\!>\!Hg$, crystallises from boiling alcohol in beautiful silvery plates, which melt at 86°. By hydric sulphide it is decomposed with re-formation of mercaptan :

$$(C_2H_5.S)_2Hg + H_2S = HgS + 2C_2H_5.SH,$$

and serves for the purification of the latter.

Aurous thio-ethylate, $C_2H_5.S.Au$, is precipitated, on mixing dilute alcoholic solutions of mercaptan and auric chloride, as a white soft mass. *Potassic thio-ethylate*, usually prepared by dissolving potassium in mercaptan :

$$2C_2H_5.SH + K_2 = H_2 + 2C_2H_5.SK,$$

crystallises in colourless needles.

Propylic thio-alcohol, $CH_3.CH_2.CH_2.SH$, boils at 67°–68°.

Isopropylic thio-alcohol, $\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CH.SH$, boils between 57° and 60°.

Butylic thio-alcohol, $CH_3.CH_2.CH_2.CH_2.SH$, boils at 98°.

Isoamylic thio-alcohol, $\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CH.CH_2.CH_2.SH$, is a colourless oil of sp. gr. ·855 at 0° and boiling at 120°.

Thio-ethers, or Sulphides of the Alcohol Radicals, $(C_nH_{2n+1})_2S$.

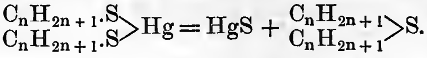
240. One method of formation of these bodies has been already given (§ 237). They are obtained in nearly theoretical quantity by the action of alkylic haloids on an alcoholic solution of potassic sulphide:

$$2C_nH_{2n+1}.Cl + K_2S = 2KCl + (C_nH_{2n+1})_2S;$$

or by distillation of a mixture of potassic sulphide with the acid sulphate of an alcohol radical:

$$2C_nH_{2n+1}.KSO_4 + K_2S = 2K_2SO_4 + (C_nH_{2n+1})_2S.$$

They are also formed by the dry distillation of mercuric mercaptides:



$$\begin{matrix}C_nH_{2n+1}.S\\C_nH_{2n+1}.S\end{matrix}{>}Hg = HgS + \begin{matrix}C_nH_{2n+1}\\C_nH_{2n+1}\end{matrix}{>}S.$$

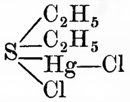
So far as known they are colourless liquids of most unpleasant odour, miscible with alcohol and ether, but not with water, and which readily take up two atoms of oxygen from oxidising agents. With metallic salts, especially those of mercury, they yield solid compounds, as also with the iodides of the alcohol radicals. They also unite directly with two atoms of the halogens.

241. *Dimethylic sulphide*, $(CH_3)_2S$, is a colourless liquid, boiling at 41° and of sp. gr. ·845. *Dimethylic sulphide-dibromide:*

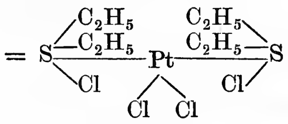
$$(CH_3)_2{=}S{=}Br_2,$$

crystallises in deliquescent octahedra.

Diethylic sulphide, $(C_2H_5)_2S$, boils at 91° and has sp. gr. ·835. In alcoholic solution it gives, with mercuric chloride, a white crystalline precipitate of the formula $(C_2H_5)_2S,HgCl_2$, probably

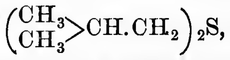


with platinic chloride, $2(C_2H_5)_2S,PtCl_4$



Dipropylic sulphide, $(CH_3.CH_2.CH_2)_2S$, boils between 130° and 135°, and has at 17° sp. gr. ·814.

Dibutylic sulphide, $(CH_3.CH_2.CH_2.CH_2)_2S$, boils at 182°.



Diisobutylic sulphide, $\left(\begin{matrix}CH_3\\CH_3\end{matrix}{>}CH.CH_2\right)_2S$, boils at 172°–173°.

Diisoamylic sulphide, $(C_5H_{11})_2S$, boils at 216°.

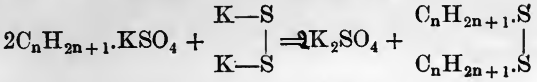
Compounds containing two different alcohol radicals have also been prepared—e.g. ethylic isoamylic sulphide, obtained by action of sodic thio-isoamylate upon ethylic iodide, or of sodic thio-ethylate upon isoamylic bromide:

$$C_2H_5.SNa + BrC_5H_{11} = NaBr + C_2H_5.S.C_5H_{11},$$

as an oil boiling between 157° and 159°.

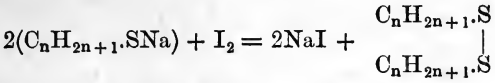
Alkylic Persulphides, $(C_nH_{2n+1})_2S_2$.

242. Persulphides of the alcohol radicals are prepared by dry distillation of potassic alkylic sulphates with K_2S_2:



$$2C_nH_{2n+1}.KSO_4 + \begin{matrix}K—S\\ |\\ K—S\end{matrix} = 2K_2SO_4 + \begin{matrix}C_nH_{2n+1}.S\\ |\\ C_nH_{2n+1}.S\end{matrix}$$

They are also obtained with great ease by action of iodine on sodic mercaptides:



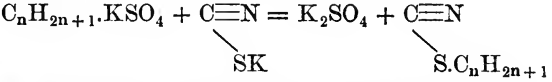
$$2(C_nH_{2n+1}.SNa) + I_2 = 2NaI + \begin{matrix}C_nH_{2n+1}.S\\ |\\ C_nH_{2n+1}.S\end{matrix}$$

Ethylic persulphide, $C_2H_5—S—S—C_2H_5$, is the best investigated of these bodies; it is a colourless liquid of nauseous odour, boils at 151°, and has nearly the same density as water.

The corresponding *isoamylic* compound, $(C_5H_{11})_2S_2$, distils at 250°.

Alkylic Sulpho-salts.

243. The alkylic salts of true sulpho-cyanic acid, $\begin{matrix}C{\equiv}N\\ \diagdown S.C_nH_{2n+1}\end{matrix}$, which are isomeric with the mustard oils, $\begin{matrix}C{=}N.C_nH_{2n+1}\\ \diagdown\!\!\diagdown S\end{matrix}$, to be described later, are obtained most readily by distillation of potassic alkylic sulphates with potassic sulpho-cyanate in aqueous solution:



$$C_nH_{2n+1}.KSO_4 + \begin{matrix}C{\equiv}N\\ \diagdown SK\end{matrix} = K_2SO_4 + \begin{matrix}C{\equiv}N\\ \diagdown S.C_nH_{2n+1}\end{matrix}$$

or by heating metallic sulpho-cyanates with alkylic iodides.

The best known is

Ethylic sulpho-cyanate, $C_2H_5.S.C{\equiv}N$, a colourless liquid, not miscible with water, which boils at 146°, and at 0° has sp. gr. 1·033. By boiling with an alcoholic solution of potassic sulphide, it yields ethylic sulphide and potassic sulpho-cyanate:

$$2N{\equiv}C—S—C_2H_5 + K_2S = 2N{\equiv}C—S—K + (C_2H_5)_2S;$$

whilst potassic hydrate decomposes it into ethylic persulphide, potassic cyanate, and potassic cyanide:

$$2N{\equiv}C—S—C_2H_5 + 2KOH = (C_2H_5)_2S_2 + N{\equiv}C—K + CONK + H_2O.$$

There are also known:

Methylic sulpho-cyanate, $CH_3.S—C{\equiv}N$, boils at 133°, sp. gr. 1·088 at 0°.

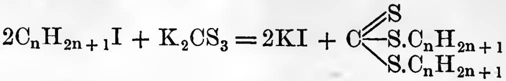
Isopropylic sulpho-cyanate, $\begin{matrix}CH_3\\ CH_3\end{matrix}\!\!>CH.S.C{\equiv}N$, boiling at 149°-151° and of sp. gr. ·963 at 20°.

Isoamylic sulpho-cyanate, $C_5H_{11}.S.C{\equiv}N$, boils at 197°, sp. gr. ·905 at 20°.

244. *Alcoholic sulpho-carbonates*, or *trisulpho-carbonates* :

$$(C_nH_{2n+1})_2CS_3,$$

result from the metallic sulpho-carbonates by action of alkylic iodides in alcoholic solution :

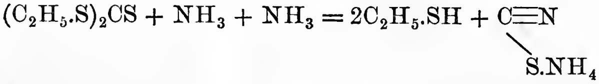


$$2C_nH_{2n+1}I + K_2CS_3 = 2KI + C\begin{array}{l} \diagup\!\!\diagup S \\ - S.C_nH_{2n+1} \\ \diagdown S.C_nH_{2n+1} \end{array}$$

They are yellowish oils of unpleasant odour.

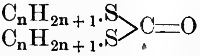
Methylic sulpho-carbonate, $(CH_3.S)_2CS$, boils at 204°–205°.

Ethylic sulpho-carbonate, $(C_2H_5S)_2CS$, boils at 237°–240°. Both are somewhat difficultly soluble in water, and decompose on heating with alcoholic ammonia into mercaptan and ammonic sulpho-cyanate :



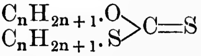
$$(C_2H_5.S)_2CS + NH_3 + NH_3 = 2C_2H_5.SH + \begin{array}{l} C{\equiv}N \\ \diagdown \\ S.NH_4 \end{array}$$

245. Between the foregoing and the alkylic carbonates there are series of bodies containing both oxygen and sulphur, the different oxy-sulpho-carbonates, $(C_nH_{2n+1})_2COS_2$ and $(C_nH_{2n+1})_2CO_2S$, and their derivatives. Each of these groups admits the possibility of isomerism :



$$\begin{array}{l} C_nH_{2n+1}.S \\ C_nH_{2n+1}.S \end{array}\!\!>C{=}O$$

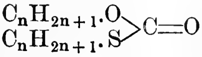
and



$$\begin{array}{l} C_nH_{2n+1}.O \\ C_nH_{2n+1}.S \end{array}\!\!>C{=}S$$

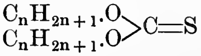
Dithio-carbonates.

Thio-oxy-sulpho-carbonates, or xanthates.



$$\begin{array}{l} C_nH_{2n+1}.O \\ C_nH_{2n+1}.S \end{array}\!\!>C{=}O$$

and



$$\begin{array}{l} C_nH_{2n+1}.O \\ C_nH_{2n+1}.O \end{array}\!\!>C{=}S$$

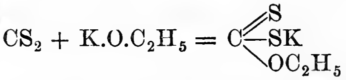
Oxy-thio-carbonate.

Dioxy-sulpho-carbonates.

The ethyl derivatives have been most investigated, and their description will suffice, the compounds of all the other alcohols, so far as they have been studied, being quite similar.

246. If a saturated alcoholic solution of potassic hydrate be mixed with carbonic disulphide, there are formed water and

Oxyethylic thio-potassic sulpho-carbonate, or *potassic xanthate* :

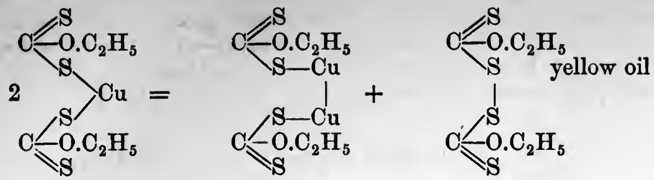


$$CS_2 + K.O.C_2H_5 = C\begin{array}{l} \diagup\!\!\diagup S \\ - SK \\ \diagdown OC_2H_5 \end{array}$$

which separates in colourless silky needles. The aqueous solution of this salt gives precipitates with the salts of the heavy metals, in which the place of the potassium is taken by the heavy metal. Its reaction with cupric salts is very characteristic ; it yields therewith at first a dark precipitate, which is without doubt a cupric salt :

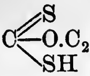
$$2C{=}S.(O.C_2H_5).S.K + CuSO_4 = [CS(O.C_2H_5).S]_2Cu + K_2SO_4,$$

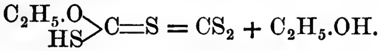
which with great rapidity, and separation of an oily body, becomes of a splendid yellow colour (therefore the name xanthate), and is now a cuprous salt :



$$2\,\begin{array}{l}\mathrm{C}{\begin{array}{l}=\mathrm{S}\\ -\mathrm{O.C_2H_5}\\ -\mathrm{S}\end{array}}\\ \mathrm{C}{\begin{array}{l}-\mathrm{S}\\ -\mathrm{O.C_2H_5}\\ =\mathrm{S}\end{array}}\end{array}\!\!>\mathrm{Cu} = \begin{array}{l}\mathrm{C}{\begin{array}{l}=\mathrm{S}\\ -\mathrm{O.C_2H_5}\\ -\mathrm{S{-}Cu}\end{array}}\\ \qquad\quad |\\ \mathrm{C}{\begin{array}{l}-\mathrm{S{-}Cu}\\ -\mathrm{O.C_2H_5}\\ =\mathrm{S}\end{array}}\end{array} + \begin{array}{l}\mathrm{C}{\begin{array}{l}=\mathrm{S}\\ -\mathrm{O.C_2H_5}\\ -\mathrm{S}\end{array}}\\ \qquad\quad |\\ \mathrm{C}{\begin{array}{l}-\mathrm{S}\\ -\mathrm{O.C_2H_5}\\ =\mathrm{S}\end{array}}\end{array}$$

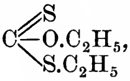
From potassic xanthate strong acids in the cold liberate

Xanthic acid,  $\mathrm{C}{\begin{array}{l}=\mathrm{S}\\ -\mathrm{O.C_2H_5}\\ -\mathrm{SH}\end{array}}$, as a colourless, acid-reacting oil, insoluble in water, which decomposes at 24° into alcohol and carbonic disulphide:



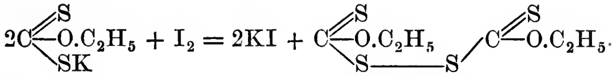
$$\begin{array}{r}\mathrm{C_2H_5.O}\\ \mathrm{HS}\end{array}\!\!>\mathrm{C{=}S} = \mathrm{CS_2} + \mathrm{C_2H_5.OH}.$$

If an alcoholic solution of potassic xanthate be mixed with an ethylic haloid, potassic haloid separates, and there is formed

Ethylic xanthate,  $\mathrm{C}{\begin{array}{l}=\mathrm{S}\\ -\mathrm{O.C_2H_5}\\ -\mathrm{S.C_2H_5}\end{array}}$, which is precipitated by water from its alcoholic solution, as a colourless oil, boiling at 212°.

On slowly adding iodine in least possible excess to an alcoholic solution of potassic xanthate, and then adding water, a precipitate is obtained of

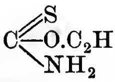
Xanthogen persulphide, $[\mathrm{CS(O.C_2H_5)}]_2\mathrm{S_2}$, as a yellowish oil, that cannot be distilled unchanged:

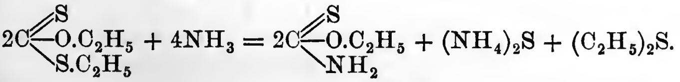


$$2\mathrm{C}{\begin{array}{l}=\mathrm{S}\\ -\mathrm{O.C_2H_5}\\ -\mathrm{SK}\end{array}} + \mathrm{I_2} = 2\mathrm{KI} + \mathrm{C}{\begin{array}{l}=\mathrm{S}\\ -\mathrm{O.C_2H_5}\\ -\mathrm{S}{-\!\!-\!\!-}\mathrm{S}\end{array}}\!\!\diagup\mathrm{C}{\begin{array}{l}=\mathrm{S}\\ -\mathrm{O.C_2H_5}.\end{array}}$$

In the pure state it forms a crystalline mass fusible at the temperature of the hand.

247. On allowing an alcoholic solution of ethylic xanthate saturated with ammonia to stand some time, and then distilling on a water bath, ammonic sulphide and ethylic sulphide pass over, and there is left a residue, becoming crystalline on cooling, of

Xanthogen amide,  $\mathrm{C}{\begin{array}{l}=\mathrm{S}\\ -\mathrm{O.C_2H_5}\\ -\mathrm{NH_2}\end{array}}$, which corresponds in composition to ethylic carbamate (§ 231):

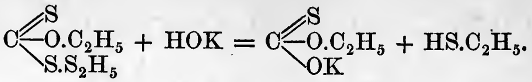


$$2\mathrm{C}{\begin{array}{l}=\mathrm{S}\\ -\mathrm{O.C_2H_5}\\ -\mathrm{S.C_2H_5}\end{array}} + 4\mathrm{NH_3} = 2\mathrm{C}{\begin{array}{l}=\mathrm{S}\\ -\mathrm{O.C_2H_5}\\ -\mathrm{NH_2}\end{array}} + \mathrm{(NH_4)_2S} + \mathrm{(C_2H_5)_2S}.$$

This body forms large colourless crystals, insoluble in water, but readily soluble in alcohol.

248. By mixing a saturated alcoholic solution of potassic hydrate with one of ethylic xanthate, colourless prismatic crystals of

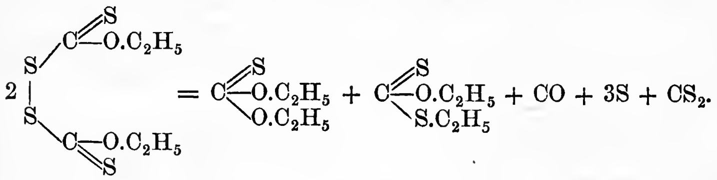
Potassic ethylic dioxy-sulpho-carbonate, $C\begin{array}{l}{=}S\\-O.C_2H_5\\-OH\end{array}$, separate, whilst mercaptan remains in solution:



$$C\begin{array}{l}{=}S\\-O.C_2H_5\\-S.S_2H_5\end{array} + HOK = C\begin{array}{l}{=}S\\-O.C_2H_5\\-OK\end{array} + HS.C_2H_5.$$

By boiling its aqueous solution this salt decomposes into potassic carbonate, alcohol, and carbonic disulphides; acids also causing the same change.

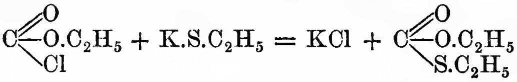
The corresponding ethylic compound, *diethylic dioxy-sulpho-carbonate,* $C\begin{array}{l}{=}S\\-O.C_2H_5\\-O.C_2H_5\end{array}$, is formed, together with ethylic xanthate, by the dry distillation of xanthogen persulphide, according to the equation:



$$2\begin{array}{l}S-C\begin{array}{l}{=}S\\-O.C_2H_5\end{array}\\ | \\ S-C\begin{array}{l}-O.C_2H_5\\{=}S\end{array}\end{array} = C\begin{array}{l}{=}S\\-O.C_2H_5\\-O.C_2H_5\end{array} + C\begin{array}{l}{=}S\\-O.C_2H_5\\-S.C_2H_5\end{array} + CO + 3S + CS_2.$$

It is a colourless oil of ethereal odour, somewhat heavier than water, and boiling at 161°.

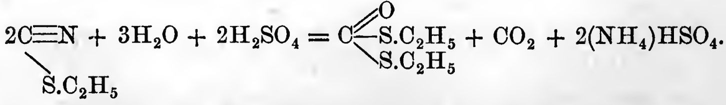
249. *Diethylic thio-oxycarbonate,* $C\begin{array}{l}{=}O\\-O.C_2H_5\\-S.C_2H_5\end{array}$, isomeric with the preceding, is obtained by the action of potassic mercaptate on ethylic chloro-carbonate:



$$C\begin{array}{l}{=}O\\-O.C_2H_5\\-Cl\end{array} + K.S.C_2H_5 = KCl + C\begin{array}{l}{=}O\\-O.C_2H_5\\-S.C_2H_5\end{array}$$

It boils at 155°–156°, and is decomposed by potassic hydrate into carbonate, ethylic alcohol, and ethylic mercaptan.

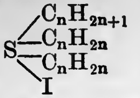
250. A compound isomeric with ethylic xanthate, *ethylic dithiocarbonate,* $C\begin{array}{l}{=}O\\-S.C_2H_5\\-S.C_2H_5\end{array}$, results from the decomposition of ethylic thiocyanate by sulphuric acid:



$$2\begin{array}{l}C\equiv N\\ \diagdown\\ S.C_2H_5\end{array} + 3H_2O + 2H_2SO_4 = C\begin{array}{l}{=}O\\-S.C_2H_5\\-S.C_2H_5\end{array} + CO_2 + 2(NH_4)HSO_4.$$

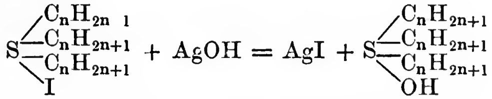
Trialkyl-sulphine Compounds.

251. The alkylic sulphides unite slowly with alcoholic iodides at ordinary temperatures, more quickly at 100°, to form colourless crystalline compounds of tetravalent sulphur of the formula



which behave as though they were the iodides of strongly positive monovalent radicals, $S(C_nH_{2n+1})_3$, and are termed trialkylic sulphine iodides. The trialkylic sulphine bromides are formed in similar manner from the thio-ethers and alcoholic bromides. These bodies are readily soluble in water and alcohol, and are decomposed when heated alone into alcoholic sulphide and iodide.

On shaking their aqueous solutions with freshly precipitated argentic oxide, the argentic haloid salt is precipitated, whilst hydrate remains in solution:



These hydrates are difficultly crystallisable bodies of strongly alkaline properties, which deliquesce in damp air. They absorb gaseous carbonic anhydride, and when mixed with metallic salts unite with the acid, precipitating the metal as hydrate. On warming with ammonic salts they expel the ammonia; e.g.

$$NH_4Cl + S(C_2H_5)_3.OH = S(C_2H_5)_3Cl + H_2O + NH_3.$$

The trialkylic sulphine salts are also formed by saturating the hydrates with acids, and react neutral. They are mostly deliquescent, soluble in alcohol but not in ether. The chlorides yield with platinic chloride soluble double salts of the formula $[S(C_nH_{2n+1})_3]_2PtCl_6$.

The ethylic compounds have been most thoroughly investigated.

Triethyl-sulphine chloride, $S.(C_2H_5)_3Cl$, forms needle-shaped crystals, yielding with platinic chloride inch-long red needles of $[S(C_2H_5)_3]_2PtCl_6$.

Triethyl-sulphine bromide, $S.(C_2H_5)_3Br$, and *triethyl-sulphine iodide*, $S(C_2H_5)_3I$, form rhombic crystals, frequently tables.

Triethyl-sulphine hydrate, $S(C_2H_5)_3.OH$, forms extremely deliquescent crystals, which attack the skin and, like potassic hydrate, dissolve precipitated alumina.

Triethyl-sulphine nitrate, $S(C_2H_5)_3O.NO_2$, crystallises in radiating deliquescent laminæ, which yield with argentic nitrate a double salt forming scaly crystals and difficultly soluble.

Trimethyl-sulphine compounds have also been prepared, such as the iodide, bromide, chloride, and hydrate, and also as a product of the action of methylic iodide on diethylic sulphide, a non-crystallisable *Diethyl-methyl sulphine iodide*, $S(C_2H_5)_2CH_3.I$.

Alkylsulphinic Acids, $C_nH_{2n+1}.SO.OH$.

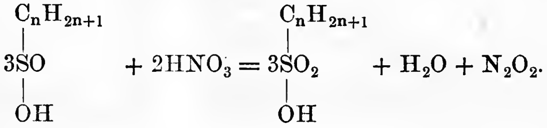
252. The zinc salts of these monobasic acids are formed by action of sulphurous anhydride upon the zinc compounds of the alcohol radicals:

$$Zn(C_nH_{2n+1})_2 + 2SO_2 = (C_nH_{2n+1}.SO.O)_2Zn.$$

The evolution of heat is so considerable during this process that the zinc organic compound must be diluted with much ether, and be well cooled during the absorption of the gas. In order to obtain the free acid the zinc salt is decomposed by baric hydrate, and the filtered baric salt solution precipitated by an equivalent quantity of sulphuric acid:

$$(C_nH_{2n+1}.SO.O)_2Ba + H_2SO_4 = BaSO_4 + 2C_nH_{2n+1}.SO.OH.$$

The acids, concentrated as far as possible by evaporation in vacuo, are acid syrups, which on heating partly decompose with separation of sulphur. By concentrated nitric acid they are oxidised to alkyl-sulphonic acids:

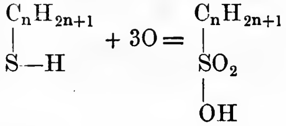


$$\begin{array}{c}C_nH_{2n+1}\\ |\\ 3SO\\ |\\ OH\end{array} + 2HNO_3 = \begin{array}{c}C_nH_{2n+1}\\ |\\ 3SO_2\\ |\\ OH\end{array} + H_2O + N_2O_2.$$

Methyl-sulphinic acid, $CH_3.SO.OH$, and *ethyl-sulphinic acid*, $C_2H_5.SO.OH$, have been prepared; the zinc salt of the latter crystallises in delicate nacreous plates of the formula $(C_2H_5.SO.O)_2Zn,H_2O$, and is rather difficultly soluble.

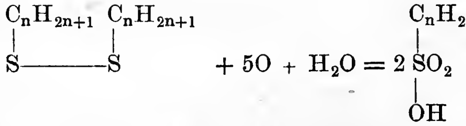
Alkylsulphonic Acids, $C_nH_{2n+1}.SO_2.OH$.

253. In the monobasic sulphonic acids the carbon of the alcohol radical, similarly to the bodies of the last group, is united to the sulphur of the acid radical, which latter is in union with hydroxyl. These compounds are obtained with great readiness by oxidation of the mercaptans:



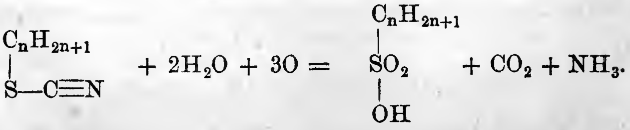
$$\begin{array}{c}C_nH_{2n+1}\\ |\\ S-H\end{array} + 3O = \begin{array}{c}C_nH_{2n+1}\\ |\\ SO_2\\ |\\ OH\end{array}$$

the alkylic persulphides:



$$\begin{array}{cc}C_nH_{2n+1} & C_nH_{2n+1}\\ | & |\\ S & \!\!\!\!-\!\!\!-\!\!\!-\!\!\!-\; S\end{array} + 5O + H_2O = 2\begin{array}{c}C_nH_{2n+1}\\ |\\ SO_2\\ |\\ OH\end{array}$$

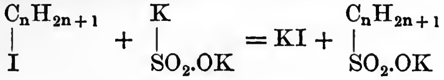
and the alkylic sulphocyanates:



$$\begin{array}{c}C_nH_{2n+1}\\ |\\ S-C\equiv N\end{array} + 2H_2O + 3O = \begin{array}{c}C_nH_{2n+1}\\ |\\ SO_2\\ |\\ OH\end{array} + CO_2 + NH_3.$$

Concentrated nitric acid is generally employed as the oxidising agent, and after long-continued action at ordinary temperatures the completion of the process assisted by heat. The solution is finally evaporated on a water bath, in order to expel all nitric acid, the residuary strongly acid liquid diluted with water and saturated with plumbic carbonate. From the filtered solution the crystalline lead salt $(C_nH_{2n+1}.SO_2.O)_2Pb$ can be obtained by evaporation, and is then decomposed in aqueous solution by sulphuretted hydrogen. The liquid, freed from plumbic sulphide by filtration, gives by evaporation on a water bath the free sulphonic acid as a strongly acid syrup, which crystallises, under a desiccator, after a while. By neutralisation by metallic carbonates the metallic salts, which are mostly readily soluble, can be obtained.

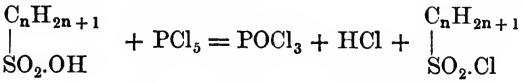
Another method of preparation consists in heating alkylic haloids with normal potassic sulphite:



$$\begin{matrix}C_nH_{2n+1}\\ |\\ I\end{matrix} + \begin{matrix}K\\ |\\ SO_2.OK\end{matrix} = KI + \begin{matrix}C_nH_{2n+1}\\ |\\ SO_2.OK\end{matrix}$$

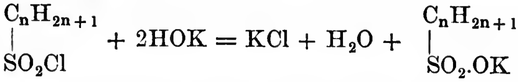
The alkylsulphonic acids are very stable compounds. They can be heated to pretty high temperatures without decomposition, are not altered by boiling with potassic hydrate, being only decomposed by fusion therewith, and are only oxidised with great difficulty by fuming nitric acid.

With phosphoric pentachloride they yield in addition to phosphoric oxychloride and hydrochloric acid the insoluble alkylic sulphonic chlorides:



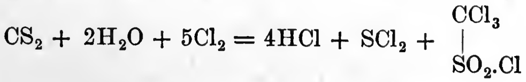
$$\begin{matrix}C_nH_{2n+1}\\ |\\ SO_2.OH\end{matrix} + PCl_5 = POCl_3 + HCl + \begin{matrix}C_nH_{2n+1}\\ |\\ SO_2.Cl\end{matrix}$$

which are reconverted into sulphonates by alkalies:



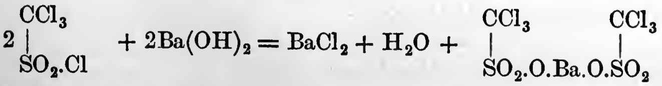
$$\begin{matrix}C_nH_{2n+1}\\ |\\ SO_2Cl\end{matrix} + 2HOK = KCl + H_2O + \begin{matrix}C_nH_{2n+1}\\ |\\ SO_2.OK\end{matrix}$$

254. *Methyl sulphonic acid*, $CH_3.SO_2.OH$, can be prepared, by the general methods given above, from methylic mercaptan, methylic disulphide, methylic sulphocyanate, and methylic haloids, and in addition from carbonic disulphide. If this latter be heated with damp chlorine or with manganic dioxide and hydrochloric acid, it slowly forms colourless crystals, melting at 135° and boiling at 170°, of *trichlormethyl sulphonic chloride:*



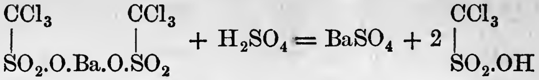
$$CS_2 + 2H_2O + 5Cl_2 = 4HCl + SCl_2 + \begin{matrix}CCl_3\\ |\\ SO_2.Cl\end{matrix}$$

Baric hydrate converts these into baric trichlormethyl sulphonate:



$$2\begin{matrix}CCl_3\\ |\\ SO_2.Cl\end{matrix} + 2Ba(OH)_2 = BaCl_2 + H_2O + \begin{matrix}CCl_3 & & CCl_3\\ | & & |\\ SO_2.O & .Ba. & O.SO_2\end{matrix}$$

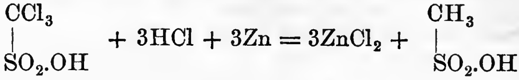
From its aqueous solution, by careful addition of sulphuric acid, the barium can be precipitated and *trichlormethyl sulphonic acid* obtained:



$$\begin{array}{l}CCl_3 \qquad\quad CCl_3\\ | \qquad\qquad\quad |\\ SO_2.O.Ba.O.SO_2\end{array} + H_2SO_4 = BaSO_4 + 2\begin{array}{l}CCl_3\\ |\\ SO_2.OH\end{array}$$

On evaporation of the filtered solution trichlormethyl sulphonic acid crystallises in colourless, deliquescent, strongly acid prisms.

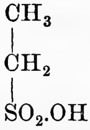
The aqueous solution, acidulated with hydrochloric acid, is submitted to the action of a strong galvanic current, the electrodes being plates of amalgamated zinc; by this means the chlorine is completely replaced by hydrogen and methyl sulphonic acid is obtained:



$$\begin{array}{l}CCl_3\\ |\\ SO_2.OH\end{array} + 3HCl + 3Zn = 3ZnCl_2 + \begin{array}{l}CH_3\\ |\\ SO_2.OH\end{array}$$

Methyl sulphonic acid is a strongly acid syrupy liquid, which on heating commences to decompose at slightly above 130°, and is only oxidised by fuming nitric acid with great difficulty.

Methyl sulphonic chloride, $CH_3.SO_2Cl$, boils at 150°–153°, and is slowly decomposed by water into hydrochloric and methyl sulphonic acids.



Ethyl sulphonic acid, $C_2H_5.SO_2.OH = \begin{array}{l}CH_3\\ |\\ CH_2\\ |\\ SO_2.OH\end{array}$, is obtained in very deliquescent crystals; its salts are all easily soluble, and can be submitted to high temperatures without decomposition.

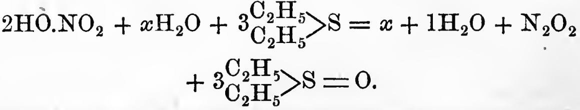
Ethyl sulphonic chloride, $C_2H_5.SO_2Cl$, boils at 171°.

Butyl sulphonic acid, $CH_3.CH_2.CH_2.CH_2.SO_2.OH$, yields a baric salt, $(C_4H_7.SO_2O)_2Ba,H_2O$, which crystallises in efflorescent tables.

Oxidation Products of the Dialkylic Sulphides.

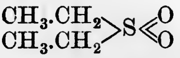
255. Whilst dimethylic sulphide, when heated with nitric acid, is in most part converted into methyl sulphonic acid, with oxidation of one methyl group, diethylic sulphide combines with the oxygen of oxidising agents, and yields peculiar oxides.

By evaporating it with dilute nitric acid a thick neutral liquid, which cannot be distilled unchanged, remains, *diethyl sulphurous oxide* or *diethyl thionyl*:



$$2HO.NO_2 + xH_2O + 3\begin{smallmatrix}C_2H_5\\ C_2H_5\end{smallmatrix}{>}S = x + 1H_2O + N_2O_2 + 3\begin{smallmatrix}C_2H_5\\ C_2H_5\end{smallmatrix}{>}S = O.$$

Strong nitric acid converts diethylic sulphide or the preceding body into *diethyl sulphone*, $(C_2H_5)_2SO_2$:



$$\begin{matrix}CH_3.CH_2\\ CH_3.CH_2\end{matrix}{>}S{\ll}\begin{matrix}O\\ O\end{matrix}$$

It crystallises in large colourless tables, which melt at 70° and distil unchanged at 248°; the substance can, however, be slowly sublimed below 100°. Nascent hydrogen, evolved from zinc and sulphuric acid, reduces diethyl sulphone to diethylic sulphide:

$$(C_2H_5)_2SO_2 + 4H = 2H_2O + (C_2H_5)_2S.$$

Dimethylic sulphide can be converted into *dimethyl thionyl* by heating its bromine compound with moist argentic oxide:

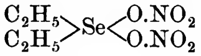
$$(CH_3)_2SBr_2 + Ag_2O = 2AgBr + (C_2H_5)_2SO.$$

SELENIUM AND TELLURIUM COMPOUNDS OF THE ALCOHOL RADICALS.

256. The compounds of the alcohol radicals with selenium and tellurium are completely analogous to those already described with sulphur.

Ethylic seleno-mercaptan, $C_2H_5.SeH$, is obtained, together with *diethylic selenide,* $(C_2H_5)_2Se$, by distillation of potassic seleno-hydrate with potassic ethylic sulphate. The first boils below 100°, and possesses a most unpleasant smell; it readily exchanges its non-radical hydrogen for mercury. Diethylic selenide is a heavy oil, boiling at 107°–108°, which unites with halogens; e.g. $(C_2H_5)_2SCl_2$.

Ethylic perselenide, $\begin{array}{l}C_2H_5\text{—Se}\\ \qquad\quad |\\ C_2H_5\text{—Se}\end{array}$, has also been prepared; it boils at 186°. Diethylic selenide is converted by treatment with nitric acid into *diethyl selenious oxide,* $(C_2H_5)_2SeO$, which yields, with excess of nitric acid, a salt of the formula $(C_2H_5)_2Se(ONO_2)_2$, or



$$\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!>Se<\!\begin{matrix}O.NO_2\\O.NO_2\end{matrix}$$

Dimethylic selenide is converted by oxidation with nitric acid into *methyl selenic acid,* $CH_3.SeO_2.OH$, which forms prisms, melting at 120°.

By mixing dialkylic selenides with alkylic iodides *trialkylic selenious iodides,* $(C_nH_{2n+1})_3SeI$, are formed, in all respects similar to the trialkylic sulphine iodides.

257. The tellurium compounds possess some further interest; derivatives corresponding to mercaptan have not yet been obtained.

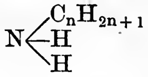
Dimethylic telluride, $(CH_3)_2Te$, is a liquid boiling at 80°–82°; on exposure to air it is oxidised to dimethyl tellurous oxide, $(CH_3)_2TeO$. By heating dimethylic telluride with nitric acid it yields dimethyl tellurous nitrate, $(CH_3)_2Te(O.NO_2)_2$, from whose solution hydrochloric acid precipitates *dimethyl tellurous dichloride,* $(CH_3)_2TeCl_2$, as a crystalline body. By treatment with argentic oxide it is converted into *dimethyl tellurous oxide.* This latter is crystalline, deliquescent, and strongly alkaline; it absorbs carbonic anhydride from the air, and decomposes ammonic salts with evolution of ammonia. With methylic iodide dimethylic telluride yields *trimethyl tellurous iodide,* $(CH_3)_3TeI$, which when treated with freshly precipitated argentic oxide is converted into the highly alkaline and very soluble *trimethyl tellurous hydrate,* $(CH_3)_3Te.OH$.

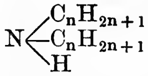
NITROGEN COMPOUNDS OF THE ALCOHOL RADICALS.

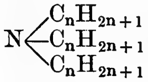
258. The most numerous class of nitrogen compounds of the alcohols correspond to ammonia and its derivations in structure and in properties; in addition the group of compounds of NO_2 with the alcohol radicals, the nitro-ethanes have been lately added.

Alkylamines.

259. The simplest nitrogen compounds of the first group are the alkylamines, i.e. ammonia in which one, two, or all three hydrogen atoms have been replaced by the same number of alcohol radicals. They may be classified into:

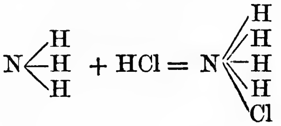
$N(C_nH_{2n+1})H_2 =$  (primary amines).

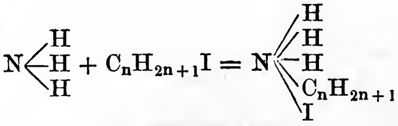
$N(C_nH_{2n+1})_2H =$  (secondary amines).

$N(C_nH_{2n+1})_3 =$  (tertiary amines).

As the alcohol radicals replacing the hydrogen in the secondary and tertiary amines may be either alike or different, the number of bodies of this kind that can be prepared is very great.

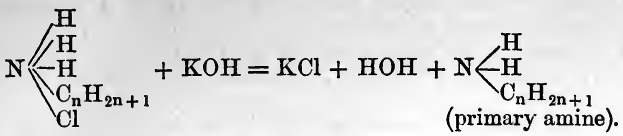
260. *Formation from Alcoholic Haloids and Ammonia.*—On bringing *ammonia* together with *alkylic haloid*, best in alcoholic solution and at a high temperature, direct union occurs. Similarly to the formation of ammonic chloride from hydrochloric acid and ammonia, there is formed by this reaction—but not with the same ease and energy—mon-alkylammonium haloid:



analogously 

or $NH_3 + C_nH_{2n+1}Cl = N(C_nH_{2n+1})H_3Cl.$

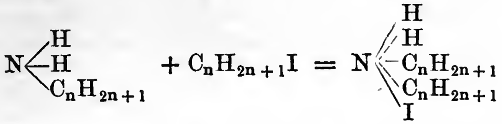
Every ammonic salt, as is well known, is decomposed by alkalies into alkaline salt, water, and ammonia, the hydroxyl group of the metallic hydrate oxidising and removing one of the four hydrogen atoms from the nitrogen compound. Alkalies act in entirely similar manner on the hydrogen of the salts of the amines. If, therefore, the salt obtained in the above reaction be boiled with potassic hydrate, there are formed potassic chloride, water, and a primary amine, which is volatile at the temperature employed:



$$N\begin{cases}H\\H\\H\\C_nH_{2n+1}\\Cl\end{cases} + KOH = KCl + HOH + N\begin{cases}H\\H\\C_nH_{2n+1}\end{cases}$$

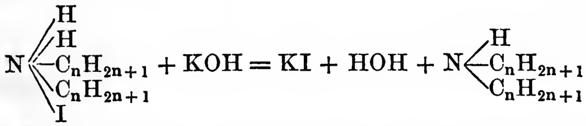
(primary amine).

If the primary amine so obtained be again mixed with an alkylic haloid, a secondary ammonic haloid is obtained:



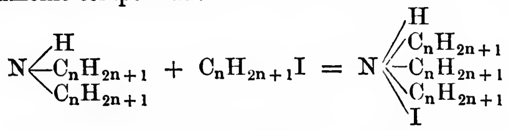
$$N\begin{cases}H\\H\\C_nH_{2n+1}\end{cases} + C_nH_{2n+1}I = N\begin{cases}H\\H\\C_nH_{2n+1}\\C_nH_{2n+1}\\I\end{cases}$$

which on warming with an alkaline hydrate yields a secondary amine:



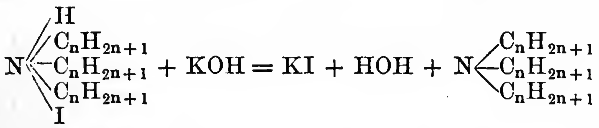
$$N\begin{cases}H\\H\\C_nH_{2n+1}\\C_nH_{2n+1}\\I\end{cases} + KOH = KI + HOH + N\begin{cases}H\\C_nH_{2n+1}\\C_nH_{2n+1}\end{cases}$$

The secondary amines further unite with alcoholic iodides, yielding trialkylammonic compounds:



$$N\begin{cases}H\\C_nH_{2n+1}\\C_nH_{2n+1}\end{cases} + C_nH_{2n+1}I = N\begin{cases}H\\C_nH_{2n+1}\\C_nH_{2n+1}\\C_nH_{2n+1}\\I\end{cases}$$

which with alkalies similarly yield potassic iodide, water, and tertiary amines:



$$N\begin{cases}H\\C_nH_{2n+1}\\C_nH_{2n+1}\\C_nH_{2n+1}\\I\end{cases} + KOH = KI + HOH + N\begin{cases}C_nH_{2n+1}\\C_nH_{2n+1}\\C_nH_{2n+1}\end{cases}$$

These processes are, however, not so simple as above represented; even in the first reaction between ammonia and the alkylic haloid complications occur which render the obtaining of pure products extremely difficult.

So soon as some primary ammonic salt has been formed, a portion of it reacts with the other substances present, so as to lead to a real substituting reaction, with formation of some dialkylammonic salt:

$$N(C_nH_{2n+1})H_3Cl + C_nH_{2n+1}.Cl + NH_3 = NH_4Cl + N(C_nH_{2n+1})_2H_2Cl;$$

and this latter is then, though only partly, converted into a tertiary ammonic chloride by a similar reaction:

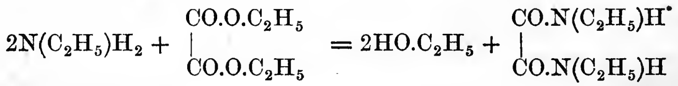
$$N(C_nH_{2n+1})_2H_2Cl + C_nH_{2n+1}Cl + NH_3 = NH_4Cl + N(C_nH_{2n+1})_3HCl;$$

If, therefore, the alkylic haloid has been completely decomposed by excess of ammonia, the product is a mixture of mono-, di-, tri-, and tetra-alkylammonium salts, from which, by distillation with potassic hydrate, a mixture of primary, secondary, and tertiary amines is obtained.

261. *Method of Preparation.*—As iodine is attached with least energy to the carbon of alcohol radicals, the alkylic iodides are nearly always used for preparing the amines. The alkylic iodide is heated to boiling with several times its volume of alcohol in a flask provided with an inverted Liebig's condenser, and dry ammonia continually passed in. The vapours rising into the condenser are thus caused to flow back into the flask. So soon as a portion of the liquid remains clear on addition of water, all the alkylic iodide has been converted. By distilling off the alcohol a dry mixture is obtained of some ammonic iodide with the iodides of the respective amines, the primary compound predominating. This is dissolved in water and distilled with potassic hydrate.

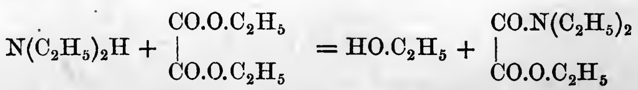
If the bromides or chlorides of the alcohol radicals be employed instead of the iodides, a higher temperature is required to complete the reaction; they are therefore heated to 100° with excess of alcoholic solution of ammonia, either in sealed tubes or, if working with large quantities, in Papin's digesters. In the case of the chlorides the ammonic chloride is found separated mostly in the crystalline state, whilst the chlorides of the amines remain dissolved in the alcohol, and by evaporation are left nearly free from ammonic salts. They therefore yield, on addition of strong solution of sodic hydrate, a mixture of the three bases free from ammonia, which on standing in closed vessels collects as a lighter layer on the top of the concentrated solution of sodic chloride.

262. The primary, secondary, and tertiary amines of low carbon contents cannot be satisfactorily separated from one another by fractional distillation. The following method is therefore employed for their separation: The mixture is dried by means of solid sodic hydrate, and then mixed with normal ethylic oxalate. This method answers especially well for the separation of the ethylamines, and they will be taken as an example. Monethylamine reacts with ethylic oxalate according to the equation:



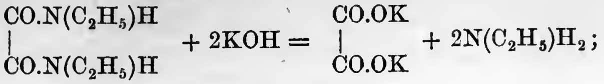
$$2N(C_2H_5)H_2 + \begin{array}{l} CO.O.C_2H_5 \\ | \\ CO.O.C_2H_5 \end{array} = 2HO.C_2H_5 + \begin{array}{l} CO.N(C_2H_5)H \\ | \\ CO.N(C_2H_5)H \end{array}$$

forming alcohol and crystalline diethyl oxamide, which is soluble in water; diethylamine, on the other hand, yielding the liquid ethylic diethyl oxamate, which boils at 250°–254°:



$$N(C_2H_5)_2H + \begin{array}{l} CO.O.C_2H_5 \\ | \\ CO.O.C_2H_5 \end{array} = HO.C_2H_5 + \begin{array}{l} CO.N(C_2H_5)_2 \\ | \\ CO.O.C_2H_5 \end{array}$$

and triethylamine remaining entirely unaltered. On distillation the latter passes over first. The diethyl oxamide and ethylic diethyl oxamate are then separated by means of warm water, and each distilled separately with potassic hydrate. The first yields ethylamine:



$$\begin{array}{l} CO.N(C_2H_5)H \\ | \\ CO.N(C_2H_5)H \end{array} + 2KOH = \begin{array}{l} CO.OK \\ | \\ CO.OK \end{array} + 2N(C_2H_5)H_2;$$

the ethylic diethyl oxamate giving diethylamine:

$$\begin{array}{l} CO.N(C_2H_5)_2 \\ | \\ CO.O.C_2H_5 \end{array} + 2KOH = \begin{array}{l} CO.OK \\ | \\ CO.OK \end{array} + HO.C_2H_5 + N(C_2H_5)_2H.$$

263. *Other Methods of Formation.*—The nitrates of the amines are formed by heating alcoholic ammonia with the nitrates of the alcohol radicals:

$$C_2H_5.O.NO_2 + NH_3 = N(C_2H_5)H_3.O.NO_2.$$

The process, however, also goes further in this case:

$$C_2H_5.O.NO_2 + NH_3 + N(C_2H_5)H_3.O.NO_2 = NH_4.O.NO_2 + N(C_2H_5)_2H_2.O.NO_2, \text{\&c.}$$

so that the same difficulty occurs here in obtaining pure products.

Some of these bodies occur naturally or result from the spontaneous decomposition, or from the dry distillation, of albuminous matters. Special methods of preparation will be given at the respective places.

264. *General Properties of the Amines.*—These bodies behave in all essential particulars like ammonia. The volatile possess an odour similar to that of ammonia, and give thick fumes with hydrochloric acid. Their aqueous solutions react strongly alkaline; they yield salts with acids without elimination of water, neutral in the case of monobasic, both acid and neutral in the case of polybasic acids:

$$N(C_nH_{2n+1})_xH_{3-x} + H_2SO_4 = (C_nH_{2n+1})_xH_{4-x}.\begin{array}{r} O \\ HO \end{array}\!\!>SO_2$$

and

$$2N(C_nH_{2n+1})_xH_{3-x} + H_2SO_4 = [N(C_nH_{2n+1})_xH_{4-x}]_2SO_4.$$

They are, generally speaking, soluble in alcohol, and are thereby distinguished from the ammonic salts, which are mostly insoluble. The hydrochloric compounds combine with platinic chloride to yellow double salts of the formula:

$$[N(C_nH_{2n+1})_xH_{4-x}]_2PtCl_6,$$

similar to ammonic platinic chloride. These latter compounds are crystalline and somewhat soluble in warm water and alcohol.

All amines, when in the state of vapour, burn in air with a continuous flame, whilst ammonia can only be got to burn continuously in pure oxygen.

As regards their basic powers, they exceed ammonia, and their positive energy increases with the number of atoms of hydrogen replaced by alcoholic radicals. Ammonia is therefore expelled from its compounds by the amines.

265. *Metamerism of the Amines.*—All alcoholic amines may be expressed by the general formula NC_nH_{2n+3}.

$$N(C_nH_{2n+1})H_2 = NC_nH_{2n+3}$$

$$N(C_{n'}H_{2n'+1})_2H = NC_{2n'}H_{4n'+2+1} = NC_nH_{2n+3} (\text{if } _{2n'} = _n).$$

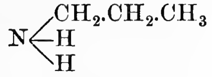
$$N(C_{n'}H_{2n'+1})(C_{n''}H_{2n''+1})H = NC_{n'+n''}H_{2n'+2n''+2+1} = NC_nH_{2n+3}$$
$$(\text{if } _{n'+n''} = _n)$$

$$N(C_{n'}H_{2n'+1})_3 = NC_{3n'}H_{2\cdot 3n'+3} = NC_nH_{2n+3} (\text{if } _{3n'} = _n).$$

$$N(C_{n'}H_{2n'+1})(C_{n''}H_{2n''+1})(C_{n'''}H_{2n'''+1})$$
$$= NC_{n'+n''+n'''}H_{2(n'+n''+n''')+3} = NC_nH_{2n+3} (\text{if } _{n'+n''+n'''} = _n).$$

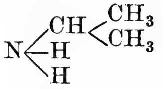
It follows from this that very numerous cases of metamerism must occur in this group, being increased by cases of true isomerism in the alcohol radicals concerned.

Whilst the formula NCH_5 corresponds to only one body, methylamine, $N(CH_3)H_2$, the formula NC_2H_7 belongs to two different bodies, ethylamine, $N(C_2H_5)H_2$, and dimethylamine, $N(CH_3)_2H$. The number of metamers and isomers increases with every additional carbon atom. Four bodies NC_3H_9 exist:



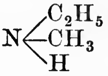
$$N\begin{cases}CH_2.CH_2.CH_3\\H\\H\end{cases}$$

Propylamine.



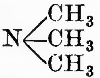
$$N\begin{cases}CH\begin{cases}CH_3\\CH_3\end{cases}\\H\\H\end{cases}$$

Isopropylamine.



$$N\begin{cases}C_2H_5\\CH_3\\H\end{cases}$$

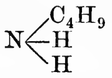
Ethyl-methyl-amine.



$$N\begin{cases}CH_3\\CH_3\\CH_3\end{cases}$$

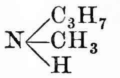
Trimethylamine.

eight NC_4H_{11}:



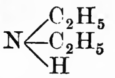
$$N\begin{cases}C_4H_9\\H\\H\end{cases}$$

Four butylamines, corresponding to the four butylic alcohols.



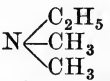
$$N\begin{cases}C_3H_7\\CH_3\\H\end{cases}$$

Two propyl-methyl-amines, corresponding to the two propylic alcohols.



$$N\begin{cases}C_2H_5\\C_2H_5\\H\end{cases}$$

Diethylamine.



$$N\begin{cases}C_2H_5\\CH_3\\CH_3\end{cases}$$

Ethyl-dimethyl-amine.

and so forth in rapidly increasing progression.

The discrimination of the individual metameric and isomeric compounds presents considerable difficulties. It can be easily determined whether an amine of a given formula is a primary, secondary, or tertiary body, but bodies of the same degree of substitution cannot generally be well distinguished from one another.

The tertiary amines are characterised by the fact that their compounds with alkylic iodides, when decomposed by potassic hydrate and distilled, yield the same body:

$$N(C_2H_5)_3 + C_2H_5I = N(C_2H_5)_4I$$

$$N(C_2H_5)_4I + KOH = KI + H_2O + N(C_2H_5)_3 + C_2H_4.$$

Secondary amines, on the contrary, by similar treatment yield a higher homologue (a compound richer in carbon and hydrogen), being converted into tertiary amines:

$$N(C_2H_5)_2H + C_2H_5I = N(C_2H_5)_3HI$$

$$N(C_2H_5)_3HI + KOH = N(C_2H_5)_3 + KI + OH_2.$$

Primary amines admit of this process of enrichment of the carbon and hydrogen contents being performed twice, and it is not until a third repetition of the process that a higher substituted body fails to be formed :

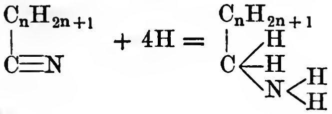
1. $N(C_2H_5)H_2 + C_2H_5I = N(C_2H_5)_2H_2I$, therefrom $N(C_2H_5)_2H$
2. $N(C_2H_5)_2H + C_2H_5I = N(C_2H_5)_3HI$ „ $N(C_2H_5)_3$
3. $N(C_2H_5)_3 + C_2H_5I = N(C_2H_5)_4I$ „ $N(C_2H_5)_3$

Primary Amines.

266. In addition to the above-given methods, primary amines can be prepared free from secondary and tertiary amines by the decomposition of alkylic isocyanates and pseudo-cyanurates (§§ 280–282) by alkalies :

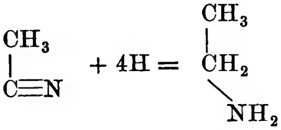
$$C_nH_{2n+1}.N{=}C{=}O + 2KOH = K_2CO_3 + C_nH_{2n+1}.NH_2\,;$$

as also by treatment of the true cyamide of the next carbon-poorer alcohol (the nitrile) with nascent hydrogen :



$$\begin{array}{l}C_nH_{2n+1}\\ \mid\\ C{\equiv}N\end{array} + 4H = \begin{array}{l}C_nH_{2n+1}\\ \mid \quad H\\ C \lessdot H\\ \quad N \lessdot {}^{H}_{H}\end{array}$$

Methylic cyanide or acetonitrile, for instance, when so treated, yields ethylamine :



$$\begin{array}{l}CH_3\\ \mid\\ C{\equiv}N\end{array} + 4H = \begin{array}{l}CH_3\\ \mid\\ CH_2\\ \quad \diagdown\\ \quad NH_2\end{array}$$

The primary amines can also be easily obtained in the pure state by reduction of the nitro-ethanes (§ 289) with nascent hydrogen.

The amines can be converted back into the alcohols by heating their hydrochlorides with potassic nitrite, there being first formed the nitrite :

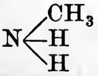
$$N(C_2H_5)H_3Cl + KONO = KCl + N(C_2H_5)H_3.O.NO,$$

which at slightly higher temperature decomposes into water, alcohol, and nitrogen :

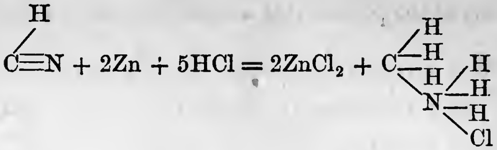
$$N(C_2H_5)H_3.O.NO = H_2O + HO.C_2H_5 + N_2\,;$$

similarly to the decomposition of ammonic nitrite :

$$NH_4.O.NO = H_2O + H_2O + N_2.$$



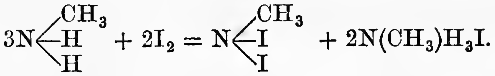
267. *Methylamine*, $CH_5N = N\begin{cases}CH_3\\ H\\ H\end{cases}$, is generally prepared from methylic isocyanate by boiling with potassic hydrate, or from prussic acid by treatment with zinc and hydrochloric acid. The methylammonic chloride formed in the last case, according to the equation



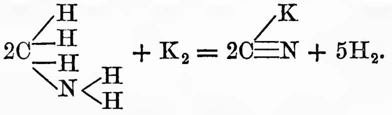
is then distilled with potassic hydrate. Methylamine is also formed by the dry distillation of various alkaloids with sodic or potassic hydrate—e.g. caffeine, theobromine, creatinine, morphine, and codeine. It is also found in coal tar and in the oily products of the distillation of animal substances (animal oil).

Methylamine is a colourless gas of intense odour, somewhat resembling that of putrefying fish. At some degrees below 0° it becomes liquid. Its vapour density is 1·08. It is easily inflammable and burns with a yellow flame; it is more soluble in water than any other gas, one volume of water at 12° absorbing 1,150 volumes of methylamine. The aqueous solution precipitates metallic salts like ammonia; if employed in excess it redissolves the hydrates of zinc and copper, but not those of cadmium, cobalt, and nickel.

Treated with the halogens, it forms bodies corresponding to the haloid compounds of nitrogen, the amide hydrogen atoms, however, being the only ones replaced by halogen. From an aqueous solution of methylamine iodine precipitates garnet-red *diiodomethylamine*, whilst methylammonic iodide remains in solution:



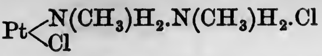
By heating with potassium it is converted into potassic cyanide with evolution of 2½ times its volume of hydrogen:



With acids it yields neutral, easily soluble salts. *Methylammonic chloride*, or *methylamine hydrochloride*, $N(CH_3)H_3Cl$, crystallises in large colourless plates, which deliquesce in moist air. It melts at a little above 100°, volatilises at a higher temperature, and condenses unaltered on cooling. The platino-chloride, $[N(CH_3)H_3]_2PtCl_6$, forms golden yellow scales, soluble in hot water, insoluble in alcohol. The auro-chloride, $N(CH_3)H_3.AuCl_4$, crystallises in golden yellow needles, readily soluble in water, alcohol, and ether.

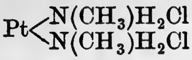
Neutral *methylammonic sulphate*, $[N(CH_3)H_3]_2SO_4$, and the *nitrate* $N(CH_3)H_3.O.NO_2$ are easily soluble in water, the latter also in alcohol.

With platinous chloride methylamine forms the salts of methylised platinum bases. At first a yellow powder of the formula $PtN_2C_2H_{10}Cl_2$ is formed, which on boiling with methylamine solution dissolves, and yields on evaporation crystals of $PtN_4C_4H_{20}Cl_2$. The first compound is the analogue either of the green salt of Magnus:



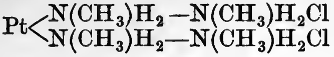
$$Pt<{N(CH_3)H_2.N(CH_3)H_2.Cl \atop Cl}$$

or of the salts of the so-called Reiset's second base (platosodiamine):

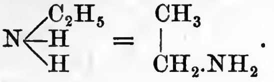


$$Pt<{N(CH_3)H_2Cl \atop N(CH_3)H_2Cl}$$

whilst the soluble second salt corresponds to Reiset's first salts (platotetramine salts):

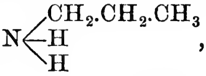


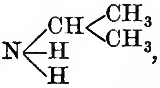
$$Pt<{N(CH_3)H_2-N(CH_3)H_2Cl \atop N(CH_3)H_2-N(CH_3)H_2Cl}$$

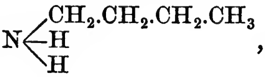
268. *Ethylamine*,  $N\begin{cases}C_2H_5\\H\\H\end{cases} = \begin{array}{l}CH_3\\|\\CH_2.NH_2\end{array}$. Ethylamine is at low temperatures a colourless, mobile liquid, of sp. gr. ·696 at 8°. It boils at + 18° and has a vapour density of 1·577. Liquid ethylamine can be mixed with water in every proportion. With metallic salts it behaves similarly to methylamine, except that in excess, like the caustic alkalies, it also dissolves aluminic hydrate. On passing chlorine gas into a dilute aqueous solution, *ethyldichloramine*, $N(C_2H_5)Cl_2$, separates as a heavy oily liquid, boiling at 91°.

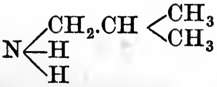
Ethylammonic chloride, $N(C_2H_5)H_3.Cl$, crystallises in deliquescent plates, which melt at 80° and boil with decomposition at 320°. It is soluble in alcohol even when containing ether. Its platino-chloride, $[N(C_2H_5)H_3]_2PtCl_6$, crystallises in orange yellow rhombohedrons. With platinous chloride it yields compounds corresponding to those described above of methylamine.

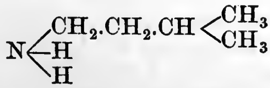
269. It will be sufficient to give the formula and boiling points of the higher homologous primary amines.

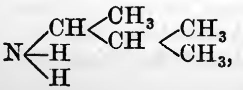
Propylamine,  $N\begin{cases}CH_2.CH_2.CH_3\\H\\H\end{cases}$, boils at 49°–50°, miscible with water.

Isopropylamine,  $N\begin{cases}CH<{CH_3 \atop CH_3}\\H\\H\end{cases}$, boils at 32°, sp. gr. ·69.

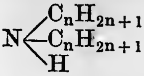
Normal butylamine,  $N\begin{cases}CH_2.CH_2.CH_2.CH_3\\H\\H\end{cases}$, boils at 76°, sp. gr. ·7401 at 20°.

Isobutylamine,  $N\begin{cases}CH_2.CH<{CH_3 \atop CH_3}\\H\\H\end{cases}$, boils at 66°–68°, sp. gr. ·7357 at 15°.

Isoamylamine,  $N\begin{cases}CH_2.CH_2.CH<{CH_3 \atop CH_3}\\H\\H\end{cases}$, boils at 95°, sp. gr. ·815.

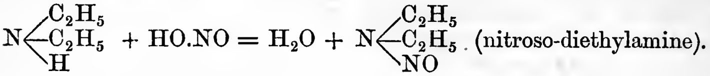
Amide of secondary isoamyl,  $N\begin{cases}CH<{CH_3 \atop CH}<{CH_3 \atop CH_3}\\H\\H\end{cases}$, boils at 78·5°, sp. gr. ·755.

Secondary Amines.



$$N\begin{cases}C_nH_{2n+1}\\C_nH_{2n+1}\\H\end{cases}$$

270. Only a few bodies of the series of secondary amines have been prepared in the pure state and thoroughly investigated. Their formation from the primary amines has been already mentioned, as has their general chemical behaviour. With nitrites they behave in completely different manner to the primary amines and ammonia. By heating their nitrites, obtained by mixing their hydrochlorides with potassic nitrite, water and a nitroso body are found. For example, if an aqueous solution of diethyl ammonic nitrite be heated, an oil, boiling at 177°, separates, which is *nitroso-diethylamine* or *nitroso-diethyline:*



$$N\begin{cases}C_2H_5\\C_2H_5\\H\end{cases} + HO.NO = H_2O + N\begin{cases}C_2H_5\\C_2H_5\\NO\end{cases} \text{(nitroso-diethylamine).}$$

Dimethylamine, $N(C_2H_5)_2H$, metameric with ethylamine, boils at between 8° and 9°. Its hydrochloride gives with platinic chloride a double salt, crystallising in beautiful needles, $[N(CH_3)_2H_2]_2PtCl_6$.

Diethylamine, $N(C_2H_5)_2H$, metameric with the butylamines, boils at 57°, and is miscible with water in every proportion.

The above-mentioned nitroso-diethylamine is converted by alcoholic potassic hydrate into monethylamine; the reaction is complicated, but may probably be represented by the equation:

$$4N(C_2H_5)_2(NO) + 8KOH = 4N(C_2H_5)H_2 + 4NH_3 + 2C_2H_4 + 4K_2CO_3.$$

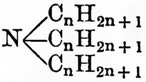
Treated with sodium amalgam, it is reconverted in presence of water into diethylamine, nitrous oxide being evolved:

$$2N(C_2H_5)_2(NO) + 4H = 2N(C_2H_5)H + H_2O + N_2O.$$

Dibutylamine, $N(CH_2.CH_2.CH_2.CH_3)_2H$, boils at 158°–160°.

Diisoamylamine, $N(C_5H_{11})_2H$, is an oily liquid, which floats on water, boils at 170°, and forms difficultly soluble salts with acids.

Tertiary Amines.



$$N\begin{cases}C_nH_{2n+1}\\C_nH_{2n+1}\\C_nH_{2n+1}\end{cases}$$

271. Nitrous acid acts with difficulty on these compounds; their nitrites also are more stable than those of the less substituted bodies.

Trimethylamine occurs ready-formed in herring pickle. From this it can be obtained mixed with ammonia by distillation with sodic hydrate. The distillate is saturated with hydrochloric acid, evaporated to dryness, and the residue extracted with strong alcohol, in which ammonic chloride dissolves but little. The filtered alcohol solution is then evaporated, and the trimethylammonic chloride distilled with potassic hydrate.

Trimethylamine also occurs in the stinking goose-foot (*Chenopo-*

dium vulvaria), in the flowers of *Crataegus oxyacantha*, in coal-tar oil, and in animal oil. It boils at + 9·3° (the metameric propylamine at 49°–50°), dissolves readily in water, and smells at once of herrings and ammonia.

Triethylamine, $N(C_2H_5)_3$, is obtained readily by heating a mixture of diethylamine and ethylic bromide; the mixture soon solidifies to fibrous crystals of triethylammonic bromide, from which triethylamine can be obtained, by distilling with an alkali, as a colourless, strongly alkaline liquid, little soluble in water. It boils at 89°. By long heating with a concentrated solution of potassic nitrite its hydrochloride is converted into nitroso-diethylamine.

Normal tributylamine, $N(CH_2.CH_2.CH_2.CH_3)_3$, is an oil boiling at 208°. *Triisoamylamine*, $N(C_5H_{11})_3$, boils at 257°.

Diethyl-isoamylamine, $N(C_2H_5)_2(C_5H_{11})$, is a mixed tertiary amine; it boils at 154°.

Methyl-ethyl-isoamylamine, $N(CH_3)(C_2H_5)(C_5H_{11})$, boils at 129°.

Tricetylamine has been obtained by slowly passing ammonia gas into cetylic iodide heated to 180°:

$$3C_{16}H_{33}I + 4NH_3 = N(C_{16}H_{33})_3 + 3NH_4I.$$

Much ammonic iodide separates, from which the melted tricetylamine is decanted; it solidifies on cooling to a crystalline mass. By repeated crystallisation from hot alcohol tricetylamine is obtained in colourless needles, which melt at 39°. Its salts, though insoluble in water, dissolve readily in alcohol and ether.

Tetralkylammonic Compounds.

272. The tetralkylammonic haloids are the last products of the action of ammonia on the haloid salts of the alcohol radicals. The iodides are generally prepared by heating a tertiary amine with an alkylic iodide to 100°. Both unite to form a crystalline compound:

$$N(C_nH_{2n+1})_3 + C_nH_{2n+1}I = N(C_nH_{2n+1})_4I,$$

which by stronger heating can be reconverted into the tertiary amine and alkylic iodide. Potassic hydrate does not exert a marked decomposing action on these bodies on boiling; by shaking their aqueous solutions with freshly precipitated argentic oxide argentic iodide separates, and the now strongly alkaline liquid contains the corresponding hydrate:

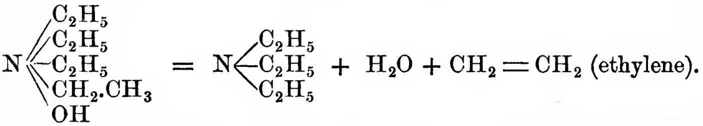
$$N(C_nH_{2n+1})_4I + AgOH = AgI + N(C_nH_{2n+1})_4.OH.$$

These hydrates behave chemically like the strongest alkalies. By evaporation in vacuo they can be obtained in crystals, which deliquesce in moist air and are caustic in strong solution. They saponify fats, precipitate metallic oxides or hydrates from metallic salts, dissolve alumina, zincic hydrate, &c., like potassic hydrate (they do not, however, dissolve chromic hydrate), and combine with the acids (even carbonic) to form salts which correspond to those of the alkalies. Their iodides unite with further quantities of iodine, forming periodides.

273. *Tetramethylammonic iodide*, $N(CH_3)_4I$, crystallises in colourless prisms, which are separated unchanged by addition of potassic hydrate to their saturated aqueous solutions, and are not decomposed even by long boiling with it. With iodine it unites to form *tetramethylammonic pentaiodide*, $N(CH_3)_4I_5$, which crystallises in brilliant metallic black crystals. *Tetramethylammonic hydrate*, prepared from the iodide by action of freshly precipitated argentic oxide, is crystalline, very deliquescent, and eagerly absorbs carbonic anhydride from the air. The nitrate $N(CH_3)_4.O.NO_2$ crystallises in long brilliant prisms. The chloride $N(CH_3)_4Cl$ gives with platinic chloride a double salt crystallising in orange yellow octahedra, $[N(CH_3)_4]_2PtCl_6$. On strong heating tetramethylammonic hydrate splits up into trimethylamine and methylic alcohol:

$$N(CH_3)_4.OH = N(CH_3)_3 + CH_3.OH.$$

274. *Tetrethylammonic iodide*, $N(C_2H_5)_4I$, is readily soluble in water and alcohol. With alcoholic solution of iodine it yields bluish black crystals of azure blue lustre of *tetrethylammonic triiodide*, $N(C_2H_5)_4I_3$, which melt at 142°. *Tetrethylammonic hydrate* crystallises in vacuo in hairlike crystals, which are very deliquescent. On heating to 100° decomposition occurs, and there is obtained triethylamine and not alcohol, but ethylene and water:



$$N\begin{cases}C_2H_5\\C_2H_5\\C_2H_5\\CH_2.CH_3\\OH\end{cases} = N\begin{cases}C_2H_5\\C_2H_5\\C_2H_5\end{cases} + H_2O + CH_2 = CH_2 \text{ (ethylene).}$$

The platino-chloride $[N(C_2H_5)_4]_2PtCl_6$ crystallises in regular octahedra.

275. The following bodies have also been obtained:

Trimethyl-ethylammonic iodide, $N(CH_3)_3(C_2H_5)I$, from trimethylamine and ethylic iodide.

Methyl-diethyl-amylic iodide, $N(CH_3)(C_2H_5)_2(C_5H_{11})I$, from methyl-diethylamine and isoamylic iodide, and *methyl-diethyl-isoamylammonic hydrate*, which on heating yields ethyl-methyl-isoamylamine, water, and ethylene:

$$N(CH_3)(C_2H_5)_2(C_5H_{11}).OH = H_2O + C_2H_4 \\ + N(CH_3)(C_2H_5)(C_2H_{11}).$$

There have further been obtained:

Triethyl-isoamylammonic hydrate from its iodide, and also *tetrisoamylammonic hydrate.*

Hydrazine Compounds.

275*a*. This name has been given to a class of bodies containing the nitrogen group $=N-N=$, whose free affinities may be saturated either with hydrogen or alcohol radicals.

They may be considered as derived from the nitro-hydride H_2N-NH_2, which has not yet, however, been isolated, by the substitution of its hydrogen by other groups.

Primary hydrazines result by the substitution of one hydrogen atom, and secondary by two of the latter. There are two isomeric forms, the symmetrically substituted and the unsymmetrically substituted group.

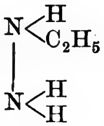
The relationship of the hydrazine series to the amines will be seen from the following list:

Amines.	*Hydrazines.*
Ethylamine, $NH_2.C_2H_5$.	Ethylhydrazine, $H_2N—NH.C_2H_5$.
Diethylamine, $NH(C_2H_5)_2$.	Diethylhydrazine, $H_2N—N.(C_2H_5)_2$.

Primary Hydrazines.

These bodies may be obtained in the fatty series from the corresponding nitroso-ureas.

275*b*. *Ethylhydrazine*, $C_2H_8N_2$ =



$$\begin{array}{l} N{<}^{H}_{C_2H_5} \\ \quad | \\ N{<}^{H}_{H} \end{array}$$

This body is best prepared from diethyl or ethyl-phenyl urea, which is converted into a nitroso compound by the action of nitrous acid, and this reduced by zinc and acetic acid, the hydrazine urea being then decomposed by some strong acid into ethylhydrazine, carbonic acid, and ethylamine, or aniline. A good process is to dissolve 50 grms. of diethyl urea in 200 cc. water, acidified with 35 grms. of sulphuric acid, and then to add to the cooled mixture the calculated quantity of sodic nitrite in small portions. The yield should be about 30 grms., which is dissolved in 180 cc. alcohol, 120 grms. zinc dust and 60 to 70 grms. glacial acetic acid added, the whole being carefully cooled. When HCl ceases to produce a precipitate of nitrosamine the liquid may be separated from the zinc dust and treated with very concentrated sodic hydrate solution, shaken out with ether, and this solution, after being acidified with HCl, evaporated.

The syrupy residue, consisting of the chlor-hydrates of diethyl carbamide and diethyl semi-carbazide, is boiled with three or four times its volume of fuming HCl, and finally saturated with HCl gas, whereby ethylhydrazine hydrochloride separates in needles.

The base is obtained in a free state by distilling the last-mentioned body with potash or baric hydrate. It is a mobile colourless liquid of ethereal odour, something like ammonia, boiling at 99·5° at 709 mm. pressure. It is soluble in water and alcohol, and very hygroscopic, and acts corrosively on cork and caoutchouc. It is very easily oxidised, and reduces alkaline copper solutions as well as silver and mercury salts in the cold. In the case of the latter metal a considerable quantity of mercury ethyl is produced. Bromine decomposes it immediately even in strongly acid solutions, liberating nitrogen. Its solutions behave towards most metallic salts like ammonia. It gives two classes of salts.

The acid hydrochlorate, $C_2H_5.N_2H_3.2HCl$, forms fine white needles, soluble in water and alcohol with decomposition into the neutral salt, $C_2H_5.N_2H_3.HCl$, which remains on evaporation as a colourless, heavy, deliquescent mass.

Secondary Hydrazines.

The unsymmetrical hydrazines of the fatty series are produced almost quantitatively by the reduction of the nitrosamines by zinc dust and acetic acid, the symmetrical hydrazines by the reduction of the corresponding azo compounds. Both varieties are simultaneously produced by the action of alkyl haloids on the primary hydrazines.

Diethylhydrazine, $(C_2H_5)_2N.NH_2$, is obtained by the careful reduction of diethyl nitrosamine with zinc and acetic acid.

After the termination of the reaction it is separated from the zinc; and the filtrate, after addition of excess of sodic hydrate, is distilled with steam, best from a copper vessel. The watery distillate, which contains hydrazine, ammonia, and diethylamine, is saturated with HCl and evaporated to remove as much ammonic chloride as possible. Hydrazine and diethylamine are separated from this filtrate on addition of potash as an oil. To separate the hydrazine the oily mixture is treated with cyanic acid, thus forming

Diethylhydrazine urea, difficultly soluble in water and alcohol, and which may thus be easily purified. It is finally distilled with solid potash or baric hydrate, and obtained as a colourless liquid of ethereal ammoniacal odour, boiling at 96°–99° and soluble in most of the ordinary solvents. It is a monacid base, and gives salts easily soluble in water and most difficult to get crystallised. With ethyl iodide it forms triethylazonium iodide:

$$(C_2H_5)_3NI—NH_2,$$

white needles easily soluble in water and alcohol, insoluble in ether.

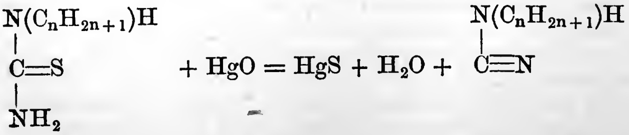
Tetrethyl tetrazon, $(C_2H_5)_2N.N = N.N.(C_2H_5)_2$. By oxidising an aqueous solution of diethylhydrazine with yellow mercuric oxide this body is obtained as a colourless oil, of an odour somewhat like leeks. It does not solidify at − 20°, and can only be distilled in a current of steam. On boiling with water it is totally decomposed. Many mixed fatty aromatic hydrazines are known, and will be described under aromatic bodies.

Alkylic Cyanamides.

276. By action of cyanogen chloride on the amines, substances analogous to the cyanamides are obtained:

$$\begin{aligned} Cl.CN + 2N(C_nH_{2n+1})H_2 &= N(C_nH_{2n+1})H_3Cl \\ &+ (CN).N(C_nH_{2n+1})H; \end{aligned}$$

as also by desulphurising the mono-alcoholic sulphureas (§ 287) by mercuric oxide in boiling aqueous or alcoholic solutions:



$$\begin{array}{l} N(C_nH_{2n+1})H \\ | \\ C{=}S \\ | \\ NH_2 \end{array} + HgO = HgS + H_2O + \begin{array}{l} N(C_nH_{2n+1})H \\ | \\ C{\equiv}N \end{array}$$

By evaporation of the liquid from which the mercuric sulphide has been filtered, they are obtained as neutral syrups, which, by repeated solution and evaporation, are readily polymerised into the crystallisable and strongly basic melamine derivatives:

$$3CN_2H(C_nH_{2n+1}) = C_3N_6H_3(C_nH_{2n+1})_3.$$

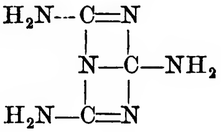
These latter can combine with two molecules of hydrochloric acid, but these salts easily decompose, with separation of ammonic chloride, into the analogous ammelide derivatives:

$$C_3N_6H_3(C_nH_{2n+1})_3,2HCl + H_2O = NH_4Cl \\ + C_3N_5.H_2(C_nH_{2n+1})_3O,HCl;$$

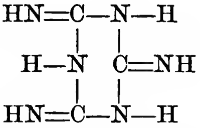
and similarly by long boiling with excess of hydrochloric acid into trialcoholic isocyanurates:

$$C_3N_6H_3(C_nH_{2n+1})_3 + 3HCl + 3H_2O = 3NH_4Cl \\ + C_3N_3.(C_nH_{2n+1})_3O_3.$$

By these reactions the melamine from which these substitution products are derived is not expressed by the formula already given (§ 117):



but only by the isomeric expression:

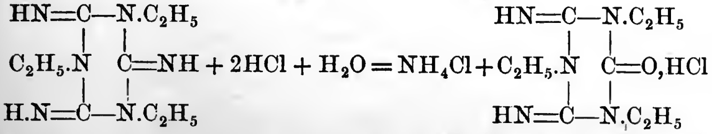


277. The most thoroughly investigated body of this class is *triethyl melamine.* This forms strongly alkaline, readily soluble, colourless crystals, whose cold concentrated hydrochloric acid solution gives with platinic chloride a double salt:

$$C_3N_6(C_2H_5)_3H_3,2HCl,PtCl_4,$$

in easily soluble, wavellite-like, crystalline masses.

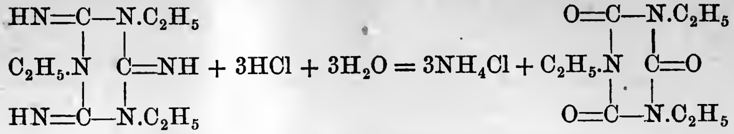
By long standing, or in shorter time by boiling its solution, triethyl melamine hydrochloride decomposes into ammonic chloride and *triethyl ammelide hydrochloride:*



from which *triethyl ammelide* can be obtained as a syrupy mass readily soluble in ether and giving with hydrochloric acid and platinic chloride the double salt

$$[C_3N_5H_2(C_2H_5)_3O]_2 2HCl,PtCl_4.$$

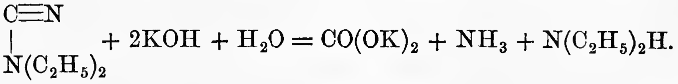
By long-continued boiling with hydrochloric acid *triethylic isocyanurate* is obtained:



If triethyl melamine be submitted to dry distillation, it splits into two compounds, of which the one remaining in the retort as an amorphous mass is by its composition a *monethyl dicyan-diamide*; the other, boiling at 190°, is *diethyl cyanamide:*

$$C_3N_6(C_2H_5)_3H_3 = \underbrace{(C_2N_2)\Big\langle\begin{smallmatrix}N(C_2H_5)H\\ NH_2\end{smallmatrix}}_{\text{Monethyl dicyan-diamide.}} + \underbrace{C_5H_{10}O_2}_{\text{Diethyl cyanamide.}}$$

The latter must be a derivative of true cyanogen, as on boiling with alkalies it yields diethylamine together with ammonia and a carbonate:



$$\begin{matrix}C\equiv N\\ |\\ N(C_2H_5)_2\end{matrix} + 2KOH + H_2O = CO(OK)_2 + NH_3 + N(C_2H_5)_2H.$$

Isocyanides of the Alcohol Radicals, $C\equiv N—C_nH_{2n+1}$.

278. The iso- or pseudo-cyanides of the alcohol radicals are formed by the action of argentic cyanide upon the iodides of the alcohol radicals (§ 96):

$$C\equiv N—Ag + IC_nH_{2n+1} = AgI + C\equiv N—C_nH_{2n+1};$$

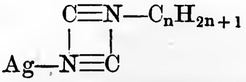
and by mixing chloroform with primary amines and an alcoholic solution of potassic hydrate:

$$CHCl_3 + N(C_nH_{2n+1})H_2 + 3KOH = 3KCl + 3H_2O$$
$$+ C\equiv N—C_nH_{2n+1}.$$

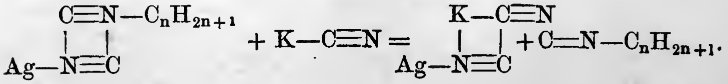
In smaller quantity they are also formed as bye-products in the preparation of the isomeric true alcoholic cyanides by dry distillation of potassic cyanide with potassic alcoholic sulphates. They are liquids difficultly soluble in water, of fearfully disagreeable odour and very poisonous properties. With argentic cyanide they unite to form crystalline bodies of the formula

$$CN.C_nH_{2n+1},CNAg,$$

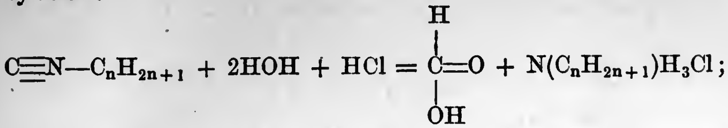
probably



from which they can be set free by heating with an aqueous solution of potassic cyanide:

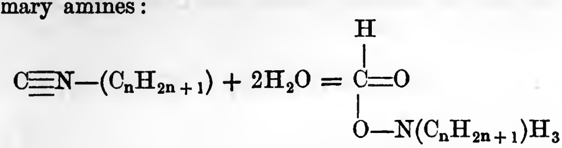


Though pretty stable towards alkali solutions, they are very readily converted into formic acid and the salts of primary monamines by acids :



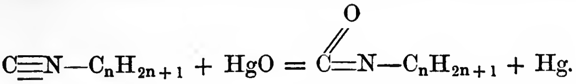
$$C\equiv N-C_nH_{2n+1} + 2HOH + HCl = \overset{H}{\underset{OH}{C}}{=}O + N(C_nH_{2n+1})H_3Cl;$$

and by long heating with water to 180° are transformed into formates of primary amines:



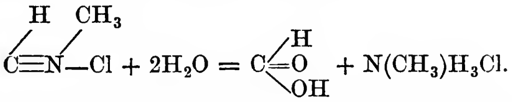
$$C\equiv N-(C_nH_{2n+1}) + 2H_2O = \overset{H}{\underset{O-N(C_nH_{2n+1})H_3}{C}}{=}O$$

By treatment with mercuric oxide they yield pseudo-cyanates (§ 280):



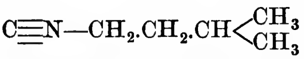
$$C\equiv N-C_nH_{2n+1} + HgO = \overset{O}{C}{=}N-C_nH_{2n+1} + Hg.$$

279. *Methylic isocyanide*, or *methyl carbammonium*, $C\equiv N-CH_3$, is a colourless liquid, which boils at 58°–59° and dissolves in ten times its weight of water. With dry hydrochloric acid it yields a solid compound, $CN.CH_3,HCl$, which by addition of water decomposes into formic acid and methylammonic chloride:



Ethylic isocyanide, or ethyl carbammonium, $C\equiv N.C_2H_5$, boils at 79° and is an oily liquid lighter than water.

Isoamylic isocyanide, or *isoamyl carbammonium :*

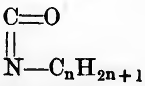


$$C\equiv N-CH_2.CH_2.CH{<}^{CH_3}_{CH_3}$$

boils at 137° and is completely insoluble in water.

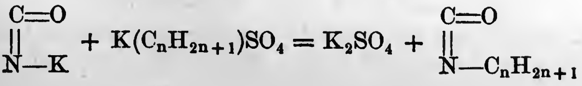
Isocyanates of the Alcohol Radicals.

280. These compounds, isomeric with the true cyanic salts (§ 234), are expressed by the general formula



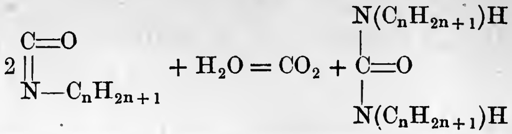
$$\begin{matrix} C{=}O \\ \| \\ N-C_nH_{2n+1} \end{matrix}$$

They are formed from the isocyanides by direct oxidation with mercuric oxide (§ 278), with greater readiness by the distillation of fused potassic cyanate with potassic alcoholic sulphates:



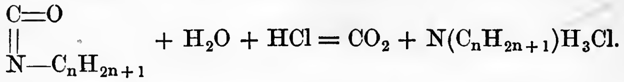
$$\begin{matrix} C{=}O \\ \| \\ N-K \end{matrix} + K(C_nH_{2n+1})SO_4 = K_2SO_4 + \begin{matrix} C{=}O \\ \| \\ N-C_nH_{2n+1} \end{matrix}$$

a larger part being invariably polymerised to isocyanurate. The known compounds are low-boiling liquids of extremely penetrating and disagreeable smell, provoking to tears; they react on water, forming carbonic anhydride and dialkyl ureas :



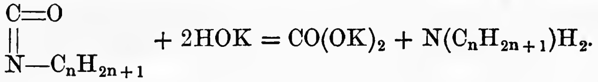
$$2\begin{array}{l}C{=}O\\ \|\\ N{-}C_nH_{2n+1}\end{array} + H_2O = CO_2 + \begin{array}{c}N(C_nH_{2n+1})H\\ |\\ C{=}O\\ |\\ N(C_nH_{2n+1})H\end{array}$$

and by aqueous acids are rapidly decomposed into carbonic anhydride and salts of primary amines:



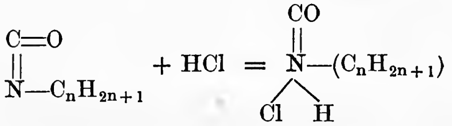
$$\begin{array}{l}C{=}O\\ \|\\ N{-}C_nH_{2n+1}\end{array} + H_2O + HCl = CO_2 + N(C_nH_{2n+1})H_3Cl.$$

With the alcohols by analogous reactions they yield primary amines (§ 266) :



$$\begin{array}{l}C{=}O\\ \|\\ N{-}C_nH_{2n+1}\end{array} + 2HOK = CO(OK)_2 + N(C_nH_{2n+1})H_2.$$

They absorb a molecule of dry hydro-acids, forming liquid compounds:

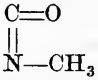


$$\begin{array}{l}C{=}O\\ \|\\ N{-}C_nH_{2n+1}\end{array} + HCl = \begin{array}{l}CO\\ \|\\ N{-}(C_nH_{2n+1})\\ \diagup\ \diagdown\\ Cl\quad H\end{array}$$

which quickly decompose with water in the above-mentioned way.

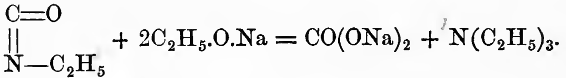
With amide compounds they unite to form substituted ureas (see §§ 282 and 283).

The following are the best known :—

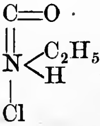


Methylic isocyanate, or *methyl-carboxyl amine*, $\begin{array}{l}C{=}O\\ \|\\ N{-}CH_3\end{array}$, a very volatile liquid.

Ethylic isocyanate, $CO(N.C_2H_5)$, boils at 60°, and with sodic ethylate yields triethylamine :



$$\begin{array}{l}C{=}O\\ \|\\ N{-}C_2H_5\end{array} + 2C_2H_5.O.Na = CO(ONa)_2 + N(C_2H_5)_3.$$



The hydrochloride, $\begin{array}{l}C{=}O\\ \|\\ N{<}^{C_2H_5}_{H}\\ |\\ Cl\end{array}$, boils at 95° and possesses a very penetrating, tear-exciting odour.

Isoamylic isocyanate, $CO(NC_5H_{11})$, boils at about 100°.

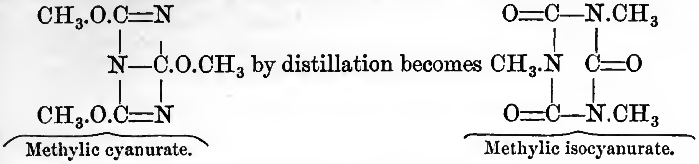
Isocyanurates of the Alcohol Radicals.

281. It has been mentioned in the preceding paragraph that in the preparation of isocyanates from potassic isocyanate and potassic alcoholic sulphates the greater part of the volatile products polymerises to isocyanurate.

By an analogous reaction the isocyanurates are also prepared by the dry distillation of potassic alkylic sulphates with tripotassic cyanurate:

$$3K(C_nH_{2n+1})SO_4 + C_3N_3O_3K_3 = 3K_2SO_4 + C_3O_3N_3(C_nH_{2n+1})_3.$$

That they result from the true cyanurates by distilling the latter, through intra-molecular change of the elements, has been already (§ 235) mentioned; e.g.



Methylic cyanurate. Methylic isocyanurate.

The formation from the trialkylic derivatives of melamine has been already given (§ 277).

The isocyanurates of the alcohol radicals, so far as they have been prepared, are crystalline bodies of pretty high melting and boiling point, and can be crystallised from hot water, alcohol, and ether. They are decomposed on boiling with alkalies (similarly to the pseudocyanates), into carbonates and primary amines:

$$C_3O_3(N.C_nH_{2n+1})_3 + 6HOK = 3CO(OK)_2 + 3N(C_nH_{2n+1})H_2.$$

The best known compounds of this series are the following:—

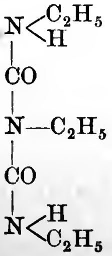
Trimethylic isocyanurate, $C_3O_3(N.CH_3)_3$, forms colourless, brilliant prismatic crystals, which melt at 175° and boil at 295°. Their vapour density is 5·92°.

Triethylic isocyanurate, $C_3O_3(N.C_2H_5)_3$, crystallises in rhombic prisms, which melt at 85° and boil at 276°.

If triethylic isocyanurate be boiled with baric hydrate solution until the precipitation of baric carbonate ceases, and the filtrate, freed from excess of baric hydrate by carbonic acid, evaporated, a viscous oil is left of the formula $C_8H_{17}N_3O_2$:

$$C_9H_{15}N_3O_3 + Ba(OH)_2 = BaCO_3 + C_8H_{17}N_3O_2.$$

This body is without doubt *triethyl biuret:*



On dry distillation it decomposes into ethylic pseudo-cyanate and diethyl urea.

In the crude triethylic isocyanurate, obtained by the dry distillation of potassic ethylic sulphate with potassic cyanurate, there is also a more readily soluble body. By boiling the mother liquor of the aqueous crystallisation with baric hydrate, and precipitation of the barium by sulphuric acid, there is obtained, on evaporation of the filtrate, hexagonal prisms, or rhombohedrons of diethylic cyanurate, $C_3N_3O_3(C_2H_5)_2H$, which melt at 173°. Its structure is as yet unknown.

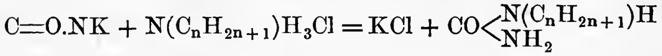
Substituted Ureas.

282. Ureas containing the alcohol radicals have not yet been prepared from urea itself, but are obtained readily from the isocyanates.

Analogously to the formation of urea from the decomposition of potassic isocyanates with ammonic salts:

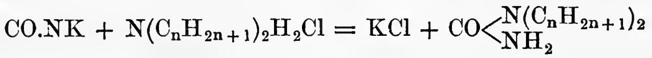
$$C{=}O.NK + NH_4Cl = KCl + CO.(NH_2)_2,$$

the former yields with the salts of primary amines the *mono-alkylic ureas:*



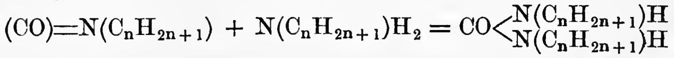
$$C{=}O.NK + N(C_nH_{2n+1})H_3Cl = KCl + CO{<}\begin{matrix}N(C_nH_{2n+1})H\\NH_2\end{matrix}$$

On decomposing potassic isocyanate with the salts of secondary amines *a-dialkylic ureas* are formed :



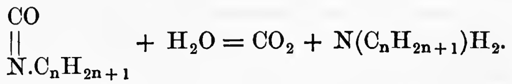
$$CO.NK + N(C_nH_{2n+1})_2H_2Cl = KCl + CO{<}\begin{matrix}N(C_nH_{2n+1})_2\\NH_2\end{matrix}$$

Metameric with these latter are β-dialkylic ureas, which are obtained from alkylic isocyanates and primary amines:



$$(CO){=}N(C_nH_{2n+1}) + N(C_nH_{2n+1})H_2 = CO{<}\begin{matrix}N(C_nH_{2n+1})H\\N(C_nH_{2n+1})H\end{matrix}$$

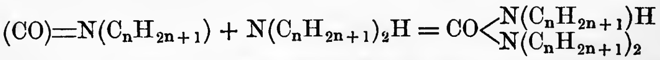
That these substituted ureas are also formed by the decomposition of the isocyanates with water has already been mentioned (§ 280). The reaction occurs without doubt in two stages, in the first according to the equation :



$$\begin{matrix}CO\\ \|\\ N.C_nH_{2n+1}\end{matrix} + H_2O = CO_2 + N(C_nH_{2n+1})H_2.$$

Together with carbonic anhydride, a primary amine is formed, which then reacts on a second molecule of the isocyanate.

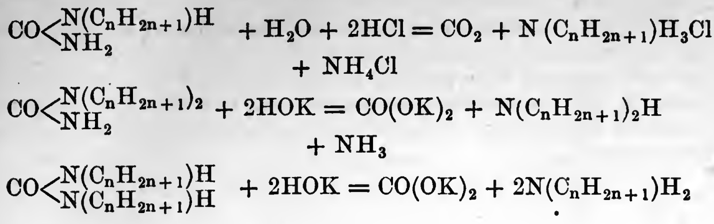
If in this latter reaction a secondary amine be used, a trisubstituted urea is obtained:



$$(CO){=}N(C_nH_{2n+1}) + N(C_nH_{2n+1})_2H = CO{<}\begin{matrix}N(C_nH_{2n+1})H\\N(C_nH_{2n+1})_2\end{matrix}$$

The tertiary amines are without action on the isocyanates of potassium and the alcohol radicals.

As by these methods polysubstituted ureas can also be prepared containing different alcohol radicals, the number of possible compounds in this group is very large. The reactions of the alkylic derivatives of urea correspond in many points with those of the parent body. They unite with acids to form saline compounds, which contain only one equivalent of the acid; by heating with aqueous acids or alkalies they are all decomposed into carbonic anhydride and amines :

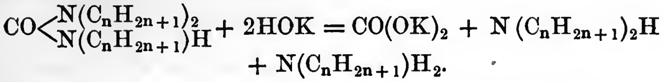


$$\mathrm{CO}{<}\genfrac{}{}{0pt}{}{N(C_nH_{2n+1})H}{NH_2} + H_2O + 2HCl = CO_2 + N(C_nH_{2n+1})H_3Cl + NH_4Cl$$

$$\mathrm{CO}{<}\genfrac{}{}{0pt}{}{N(C_nH_{2n+1})_2}{NH_2} + 2HOK = CO(OK)_2 + N(C_nH_{2n+1})_2H + NH_3$$

$$\mathrm{CO}{<}\genfrac{}{}{0pt}{}{N(C_nH_{2n+1})H}{N(C_nH_{2n+1})H} + 2HOK = CO(OK)_2 + 2N(C_nH_{2n+1})H_2$$

and finally

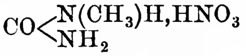


$$\mathrm{CO}{<}\genfrac{}{}{0pt}{}{N(C_nH_{2n+1})_2}{N(C_nH_{2n+1})H} + 2HOK = CO(OK)_2 + N(C_nH_{2n+1})_2H + N(C_nH_{2n+1})H_2.$$

At higher temperatures, however, they show a difference in behaviour. The mono derivatives, similarly to urea, cannot be distilled unchanged, but give primary amines and cyanuric acid, whilst the di and tri derivatives distil unaltered.

283. The following are the more important of the numerous compounds known :—

Methyl urea, $H_2N—CO—N(CH_3)H$, forms long prisms, deliquescent in moist air, from whose concentrated solution nitric acid separates a difficultly soluble nitrate of the formula :



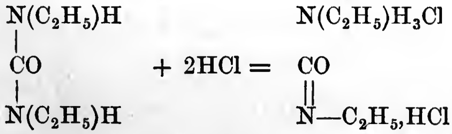
$$\mathrm{CO}{<}\genfrac{}{}{0pt}{}{N(CH_3)H,HNO_3}{NH_2}$$

Ethyl urea, $H_2N—CO—N(C_2H_5)H$, crystallises in readily soluble long prisms, which melt at 92° and decompose at about 200°. The nitrate is readily soluble.

a-Diethyl urea, $H_2N—CO—N(C_2H_5)_2$, prepared from potassic isocyanate and diethylammonic salts, is metameric with β-diethyl urea.

β-Dimethyl urea, $H(CH_3)N—CO—N(CH_3)H$, melts at 97° and boils unaltered at 270°–280°.

β-Diethyl urea, $H(C_2H_5)N—CO—N(C_2H_5)H$, crystallises in large prisms, which melt at 112°–113° and boil at 263° without decomposition. When heated in an atmosphere of dry hydrochloric acid, it splits up into ethylammonic chloride and ethylic pseudo-cyanate hydrochloride (§ 280) :



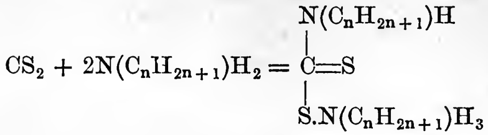
$$\begin{matrix} N(C_2H_5)H \\ | \\ CO \\ | \\ N(C_2H_5)H \end{matrix} + 2HCl = \begin{matrix} N(C_2H_5)H_3Cl \\ \\ CO \\ \| \\ N—C_2H_5,HCl \end{matrix}$$

Of the numerous analogous compounds with different alcohol radicals *methyl-ethyl urea* may be mentioned; it is very deliquescent and is prepared by action of methylamine on ethylic isocyanate.

Triethyl urea, $H(C_2H_5)N—CO—N(C_2H_5)_2$, is soluble in water, alcohol, and ether, melts at 63°, and distils unchanged at 223°.

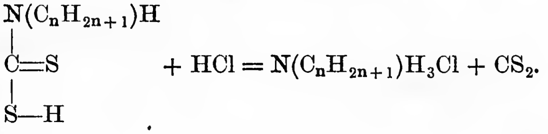
Thiocarb-alkylamine Compounds.

284. The alkylamine compounds of the thio-carbonic acid radical CS are more thoroughly known than those of carboxyl. If an alcoholic solution of a primary amine be mixed with carbonic disulphide they unite with evolution of heat, and on evaporating the solutions the primary amine salts of the alkylic sulpho-carbamates are obtained:



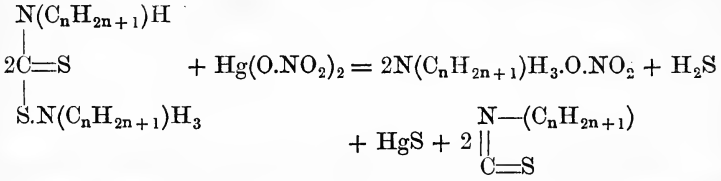
$$CS_2 + 2N(C_nH_{2n+1})H_2 = \begin{array}{l} N(C_nH_{2n+1})H \\ | \\ C{=}S \\ | \\ S.N(C_nH_{2n+1})H_3 \end{array}$$

from which acids precipitate the mono-substituted sulpho-carbamic acid as oils which solidify to crystalline masses. In the presence of excess of acid these decompose with evolution of carbonic disulphide:



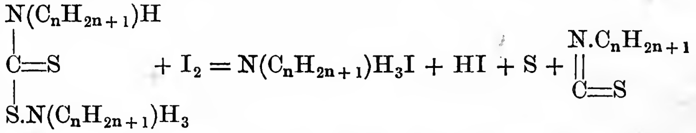
$$\begin{array}{l} N(C_nH_{2n+1})H \\ | \\ C{=}S \\ | \\ S{-}H \end{array} + HCl = N(C_nH_{2n+1})H_3Cl + CS_2.$$

If the original salts be heated with argentic or mercuric salts, metallic sulphide is precipitated, sulphuretted hydrogen evolved, and isosulpho-cyanates (so-called mustard oils) formed:



$$2\begin{array}{l} N(C_nH_{2n+1})H \\ | \\ C{=}S \\ | \\ S.N(C_nH_{2n+1})H_3 \end{array} + Hg(O.NO_2)_2 = 2N(C_nH_{2n+1})H_3.O.NO_2 + H_2S + HgS + 2\begin{array}{l} N{-}(C_nH_{2n+1}) \\ \| \\ C{=}S \end{array}$$

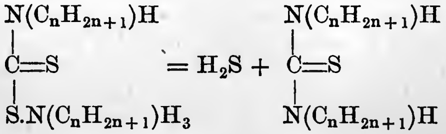
The conversion is still easier if iodine tincture be employed instead:



$$\begin{array}{l} N(C_nH_{2n+1})H \\ | \\ C{=}S \\ | \\ S.N(C_nH_{2n+1})H_3 \end{array} + I_2 = N(C_nH_{2n+1})H_3I + HI + S + \begin{array}{l} N.C_nH_{2n+1} \\ \| \\ C{=}S \end{array}$$

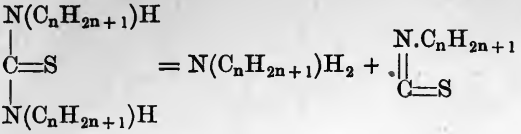
The separated sulphur is filtered off and the liquid distilled with sodic hydrate, when the isosulpho-cyanate distils.

If the alkylamic salts of sulpho-carbamic acids be heated, they evolve hydric sulphide and leave disubstituted sulphureas:



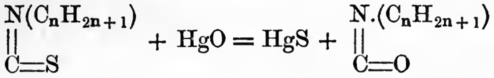
$$\begin{array}{l} N(C_nH_{2n+1})H \\ | \\ C{=}S \\ | \\ S.N(C_nH_{2n+1})H_3 \end{array} = H_2S + \begin{array}{l} N(C_nH_{2n+1})H \\ | \\ C{=}S \\ | \\ N(C_nH_{2n+1})H \end{array}$$

which by distillation with phosphoric anhydride are converted into isosulpho-cyanates:



$$\begin{array}{l} N(C_nH_{2n+1})H \\ | \\ C{=}S \\ | \\ N(C_nH_{2n+1})H \end{array} = N(C_nH_{2n+1})H_2 + \begin{array}{l} N.C_nH_{2n+1} \\ \| \\ C{=}S \end{array}$$

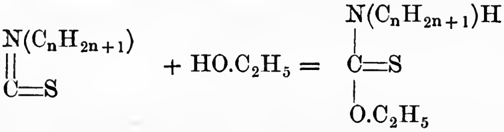
285. The alkylic isosulpho-cyanates are distillable liquids of strong, tear-exciting odour, which raise blisters on the skin. By boiling their alcoholic solutions with mercuric oxide they are converted into the corresponding isocyanates:



$$\begin{array}{l} N(C_nH_{2n+1}) \\ \| \\ C{=}S \end{array} + HgO = HgS + \begin{array}{l} N.(C_nH_{2n+1}) \\ \| \\ C{=}O \end{array}$$

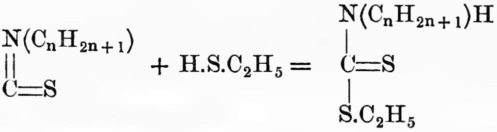
which soon undergo further change.

If an isosulpho-cyanate be heated with absolute alcohol to 110°–120° it is converted into ethylic alkyl-oxysulpho-carbamate:



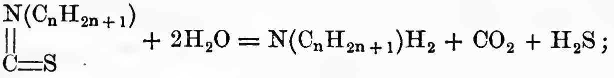
$$\begin{array}{l} N(C_nH_{2n+1}) \\ \| \\ C{=}S \end{array} + HO.C_2H_5 = \begin{array}{l} N(C_nH_{2n+1})H \\ | \\ C{=}S \\ | \\ O.C_2H_5 \end{array}$$

whilst by mercaptan in analogous reaction ethylic alkyl-disulpho-carbamates are formed:



$$\begin{array}{l} N(C_nH_{2n+1}) \\ \| \\ C{=}S \end{array} + H.S.C_2H_5 = \begin{array}{l} N(C_nH_{2n+1})H \\ | \\ C{=}S \\ | \\ S.C_2H_5 \end{array}$$

By heating with water to 200° the isosulpho-cyanates are decomposed into amines, hydric sulphide, and carbonic anhydride:

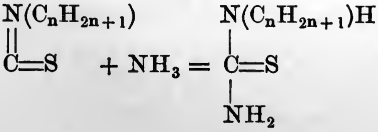


$$\begin{array}{l} N(C_nH_{2n+1}) \\ \| \\ C{=}S \end{array} + 2H_2O = N(C_nH_{2n+1})H_2 + CO_2 + H_2S;$$

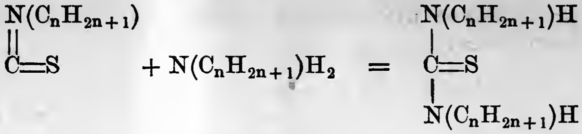
by concentrated sulphuric acid with evolution of carbonic oxysulphide:

$$CS(N.C_nH_{2n+1}) + H_2SO_4 + H_2O = [N(C_nH_{2n+1})H_3]HSO_4 + COS.$$

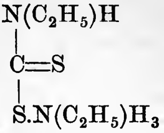
They unite very readily with ammonia and with amines to form sulphureas:

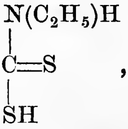


$$\begin{array}{l} N(C_nH_{2n+1}) \\ \| \\ C{=}S \end{array} + NH_3 = \begin{array}{l} N(C_nH_{2n+1})H \\ | \\ C{=}S \\ | \\ NH_2 \end{array}$$

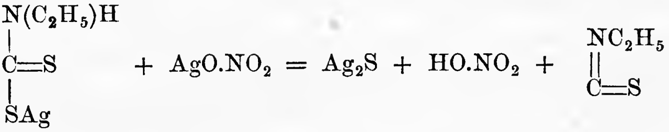


$$\begin{array}{l} N(C_nH_{2n+1}) \\ \| \\ C{=}S \end{array} + N(C_nH_{2n+1})H_2 = \begin{array}{l} N(C_nH_{2n+1})H \\ | \\ C{=}S \\ | \\ N(C_nH_{2n+1})H \end{array}$$

286. The ethyl compounds of this group are best known. Ethylamine unites with carbonic disulphide to form *Ethylammonic ethyl-sulpho-carbamate,*  $\begin{array}{l} N(C_2H_5)H \\ | \\ C{=}S \\ | \\ S.N(C_2H_5)H_3 \end{array}$, which crystallises in beautiful hexagonal tables, melting at 103°.

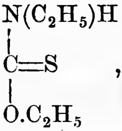
Ethyl sulpho-carbamic acid,  $\begin{array}{l} N(C_2H_5)H \\ | \\ C{=}S \\ | \\ SH \end{array}$, prepared from this, is at first obtained as an oil, which after a time becomes crystalline.

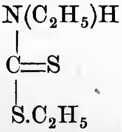
By boiling its argentic salt with a slight excess of argentic nitrate ethylic isosulpho-cyanate is obtained as a colourless liquid, boiling at 134°:



$$\begin{array}{l} N(C_2H_5)H \\ | \\ C{=}S \\ | \\ SAg \end{array} + AgO.NO_2 = Ag_2S + HO.NO_2 + \begin{array}{l} NC_2H_5 \\ \| \\ C{=}S \end{array}$$

It is more generally prepared from ethylammonic ethyl-sulpho-carbamate by action of tincture of iodine.

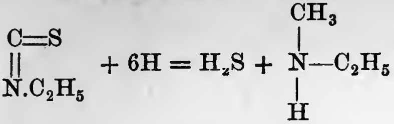
Absolute alcohol unites at 110° with ethylic isosulpho-cyanate, forming *Ethylic ethyl-sulpho-oxycarbamate,*  $\begin{array}{l} N(C_2H_5)H \\ | \\ C{=}S \\ | \\ O.C_2H_5 \end{array}$, an oil smelling like garlic, which boils unaltered at 204°–208°.

Ethylic mercaptan converts ethylic isosulpho-cyanate into *Ethylic ethyl-sulpho-carbamate,*  $\begin{array}{l} N(C_2H_5)H \\ | \\ C{=}S \\ | \\ S.C_2H_5 \end{array}$, which is resolved into its components on distillation.

If ethylic isosulpho-cyanate be treated with zinc and hydrochloric acid, it is in part converted into ethylamine and methene sulphide:

$$CS(N.C_2H_5) + 4H = N.C_2H_5.H_2 + CSH_2\,;$$

whilst another part yields methyl-ethyl-amine and hydric sulphide :

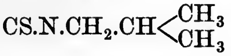


$$\begin{array}{l}C{=}S\\ \|\\ N.C_2H_5\end{array} + 6H = H_2S + \begin{array}{l}CH_3\\ |\\ N{-}C_2H_5\\ |\\ H\end{array}$$

The following isosulpho-cyanates of alcohol radicals are also known :—

Methylic isosulpho-cyanate, $CS(N.CH_3)$, a crystalline solid, which melts at 34°, boils at 119°, and smells strongly like horse radish.

Butylic Isosulpho-cyanates.—Isobutylic isosulpho-cyanate :



$$CS.N.CH_2.CH{<}\begin{array}{l}CH_3\\ CH_3\end{array}$$

is prepared by the methods given above. It is liquid and boils at 161°–163°. Another butylic salt forms the chief constituent of the ethereal oil of scurvy grass (*Cochlearia officinalis*). It boils at 159°–160°, and yields with ammonia a different urea to that given by the first.

Isoamylic isosulpho-cyanate, $CSN.CH_2.CH_2.CH{<}\begin{array}{l}CH_3\\ CH_3\end{array}$, is an oily liquid, boiling at 183°–184°.

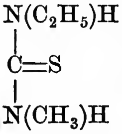
287. *Substituted Sulphureas.—Diethyl-sulphurea*, $CS(N.C_2H_5.H)_2$, prepared by heating ethylammonic ethyl-sulpho-carbamate, and by union of ethylic isosulpho-cyanate with ethylamine, forms large crystals, which melt at 77°. Their aqueous solution gives with platinic chloride a bright yellow crystalline precipitate.

On boiling the alcoholic solution with mercuric oxide β-diethyl urea is formed :

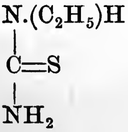
$$CS(N.C_2H_5.H)_2 + HgO = HgS + CO(N.C_2H_5.H)_2.$$

By heating in an atmosphere of hydrochloric acid, it is decomposed (analogously to diethyl urea) into ethylammonic chloride and ethylic isosulpho-cyanate :

$$CS(N.C_2H_5.H) + HCl = N.C_2H_5.H_3Cl + CS(NC_2H_5).$$

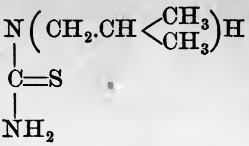


Ethyl-methyl sulphurea, $\begin{array}{l}N(C_2H_5)H\\ |\\ C{=}S\\ |\\ N(CH_3)H\end{array}$, is prepared from ethylic isosulpho-cyanate and methylamine.

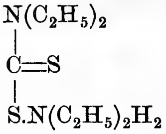


Ethyl sulphurea, $\begin{array}{l}N.(C_2H_5)H\\ |\\ C{=}S\\ |\\ NH_2\end{array}$, forms colourless needles, which melt at 89°.

By boiling its alcoholic solution with mercuric oxide, HgS and H_2O are formed, together with ethyl cyanamide, which polymerises into triethyl melamine (§ 276).

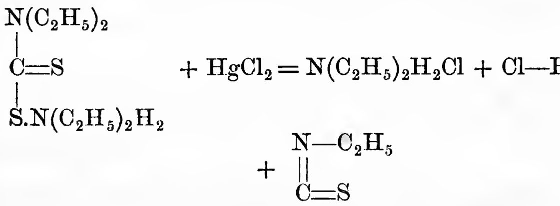
Isobutyl sulphurea,  $\begin{array}{l} N\left(CH_2.CH<^{CH_3}_{CH_3}\right)H \\ | \\ C{=}S \\ | \\ NH_2 \end{array}$, obtained from isobutylic isosulpho-cyanate and ammonia, melts at 90°, whilst that prepared from the scurvy grass butylic isosulpho-cyanate melts at 135°.

On bringing carbonic disulphide and diethylamine together in alcoholic solution, they unite to form *diethylammonic diethyl-sulphocarbamate:*



$$\begin{array}{l} N(C_2H_5)_2 \\ | \\ C{=}S \\ | \\ S.N(C_2H_5)_2H_2 \end{array}$$

The solution of this salt, when boiled with mercuric oxide, gives ethylic isosulpho-cyanate and chlor-mercuric sulpho-ethylate:

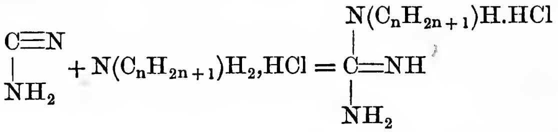


$$\begin{array}{l} N(C_2H_5)_2 \\ | \\ C{=}S \\ | \\ S.N(C_2H_5)_2H_2 \end{array} + HgCl_2 = N(C_2H_5)_2H_2Cl + Cl{-}Hg{-}S{-}C_2H_5 + \begin{array}{l} N{-}C_2H_5 \\ \| \\ C{=}S \end{array}$$

No sulphureas can be prepared from tertiary amines.

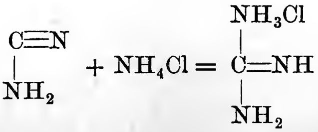
Substituted Guanidines.

288. The monosubstituted derivative $CN_3(C_nH_{2n+1})H_4$ can be prepared by heating cyanamide with the hydrochlorides of primary amines:



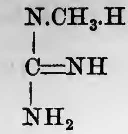
$$\begin{array}{l} C{\equiv}N \\ | \\ NH_2 \end{array} + N(C_nH_{2n+1})H_2,HCl = \begin{array}{l} N(C_nH_{2n+1})H.HCl \\ | \\ C{=}NH \\ | \\ NH_2 \end{array}$$

similarly to the formation of guanidine by action of cyanamide on ammonic salts:



$$\begin{array}{l} C{\equiv}N \\ | \\ NH_2 \end{array} + NH_4Cl = \begin{array}{l} NH_3Cl \\ | \\ C{=}NH \\ | \\ NH_2 \end{array}$$

By this method methyl guanidine hydrochloride is prepared, from which, by treatment with argentic oxide, *methyl guanidine:*



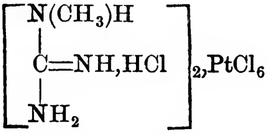
$$\begin{array}{l} N.CH_3.H \\ | \\ C{=}NH \\ | \\ NH_2 \end{array}$$

can be separated.

Methyl guanidine had been known for a long time, under the name of *methyl uramine*, as a product of the action of mercuric oxide upon creatine and creatinine.

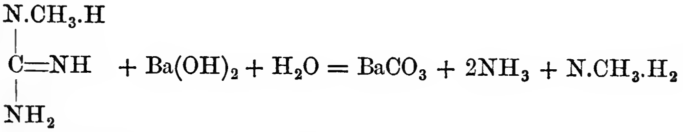
It forms a colourless, crystalline, deliquescent mass of strongly alkaline reaction and caustic ammoniacal taste. It decomposes ammonic salts, precipitates metallic oxide from their salts, dissolves aluminic and ferric hydrates, and absorbs carbonic anhydride from the air.

Its crystalline salts contain one equivalent of acid and react slightly alkaline. The hydrochloride yields with platinic chloride a double salt, crystallising in the monoclinic system and of the formula:



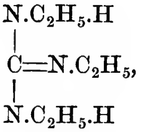
$$\left[\begin{array}{l} N(CH_3)H \\ | \\ C{=}NH,HCl \\ | \\ NH_2 \end{array}\right]_2,PtCl_6$$

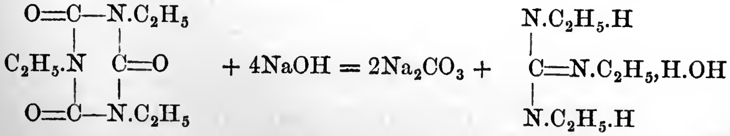
On boiling with solution of baric hydrate it decomposes into carbonate, ammonia, and methylamine:



$$\begin{array}{l} N.CH_3.H \\ | \\ C{=}NH \\ | \\ NH_2 \end{array} + Ba(OH)_2 + H_2O = BaCO_3 + 2NH_3 + N.CH_3.H_2$$

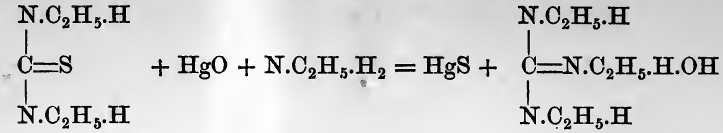
Disubstituted derivatives have not yet been prepared, but tri derivatives are known.

Triethyl guanidine,  $\begin{array}{l} N.C_2H_5.H \\ | \\ C{=}N.C_2H_5, \\ | \\ N.C_2H_5.H \end{array}$ is obtained from triethylic isocyanurate (§ 281) by heating with an alcoholic solution of sodic ethylate, and separates, in union with water, as a hydrate forming a strongly alkaline oil:



$$\begin{array}{l} O{=}C{-}N.C_2H_5 \\ \quad | \qquad | \\ C_2H_5.N \quad C{=}O \\ \quad | \qquad | \\ O{=}C{-}N.C_2H_5 \end{array} + 4NaOH = 2Na_2CO_3 + \begin{array}{l} N.C_2H_5.H \\ | \\ C{=}N.C_2H_5,H.OH \\ | \\ N.C_2H_5.H \end{array}$$

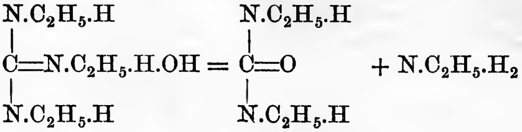
It is also obtained by boiling an alcoholic solution of diethyl sulphurea containing much ethylamine with mercuric oxide:



$$\begin{array}{l}N.C_2H_5.H\\ |\\ C{=}S\\ |\\ N.C_2H_5.H\end{array} + HgO + N.C_2H_5.H_2 = HgS + \begin{array}{l}N.C_2H_5.H\\ |\\ C{=}N.C_2H_5.H.OH\\ |\\ N.C_2H_5.H\end{array}$$

It absorbs carbonic anhydride from the air, and yields salts with acids. The platino-chloride $2[CSN_3(C_2H_5)_3H_2.HCl]_2,PtCl_4$ crystallises in beautiful tables.

On distilling hydrated triethyl guanidine, it decomposes into ethylamine and diethyl urea:



$$\begin{array}{l}N.C_2H_5.H\\ |\\ C{=}N.C_2H_5.H.OH\\ |\\ N.C_2H_5.H\end{array} = \begin{array}{l}N.C_2H_5.H\\ |\\ C{=}O\\ |\\ N.C_2H_5.H\end{array} + N.C_2H_5.H_2$$

Nitro-paraffins, $C_nH_{2n+1}.NO_2$.

289. These compounds, isomeric with the alkylic nitrites (§ 213), are readily obtained by the action of alkylic iodides upon argentic nitrite, which, therefore, probably in great part, is not the salt Ag—O—NO, but $Ag—NO_2$. The reaction goes on with great violence according to the equation:

$$C_nH_{2n+1}I + AgNO_2 = AgI + C_nH_{2n+1}.NO_2.$$

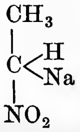
The nitro-paraffin is distilled from the argentic iodide and purified by fractionation.

The nitro-paraffins are distinguished from the isomeric alcoholic nitrites by their much higher boiling points and greater stability. They do not explode on heating. A property peculiar to those poorer in carbon (it ceases with the butyl compounds) is their power of exchanging one atom of hydrogen for sodium, this occurring either by action of the metal on ethereal solution of the nitro-paraffin or by treatment with sodic hydrate in water or alcohol:

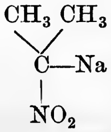
$$2C_nH_{2n+1}.NO_2 + Na_2 = H_2 + 2C_nH_{2n}Na.NO_2.$$
$$C_nH_{2n+1}.NO_2 + NaOH = OH_2 + C_nH_{2n}Ha.NO_2.$$

This first reaction by employment of potassium becomes so energetic that the mixture inflames.

In these compounds the alkali metal invariably attaches itself to that carbon atom to which the NO_2 group is united:



Sodium nitro-ethane.



Sodium nitro-isopropane.

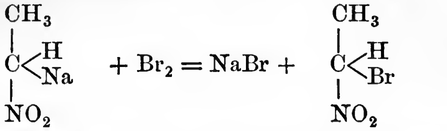
On heating the dry metallic compounds they explode violently. In water they are readily soluble, but then easily decompose; in alcohol the sodium compounds are insoluble, the potassium compounds soluble and readily changed.

If the fresh aqueous solution of a sodium compound be acidulated, the nitro-paraffin separates unchanged as an oil; if mixed with salts of heavy metals, the latter replace the sodium. These resulting metallic nitro-paraffins are mostly insoluble precipitates. The silver compounds, for instance:

$$C_nH_{2n}Na(NO_2) + AgO.NO_2 = NaO.NO_2 + C_nH_{2n}Ag(NO)_2,$$

are curdy precipitates, which rapidly blacken, owing to separation of silver.

When the fresh aqueous solutions of sodium or potassium nitro-paraffins (obtained by solution of nitro-paraffins in concentrated solutions of the respective hydrates) are slowly mixed with bromine, the brom-nitro-paraffins separate as distillable oils; e.g.



$$\begin{matrix} CH_3 \\ | \\ C{<}^{H}_{Na} \\ | \\ NO_2 \end{matrix} + Br_2 = NaBr + \begin{matrix} CH_3 \\ | \\ C{<}^{H}_{Br} \\ | \\ NO_2 \end{matrix}$$

Sodium nitro-ethane. Brom-nitro-ethane.

There is invariably, however, some dibrom-nitro-ethane:

$$CH_3.CBr_2NO_2,$$

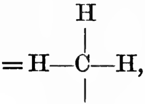
obtained at the same time.

By treatment of a slightly heated alcoholic solution of a nitro-paraffin with acetic acid and iron filings, reduction to the acetate of a primary amine occurs:

$$(C_nH_{2n+1})NO_2 + 3Fe + 7HO.C_2H_3O = 3Fe(O.C_2H_3O)_2 + 2H_2O$$
$$+ (C_nH_{2n+1})NH_3.O.C_2H_3O,$$

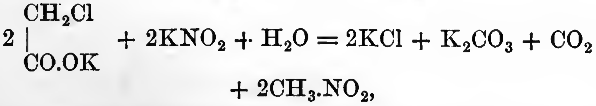
from which on distillation with an alkali the primary amine is obtained.

290. The following compounds have so far been obtained:—



Nitro-methane, $CH_3.NO_2 = \begin{matrix} H \\ | \\ H\text{—}C\text{—}H \\ | \\ O{=}N{=}O \end{matrix}$, a colourless mobile liquid little soluble in water and which boils at 99°–101°.

It is also obtained by heating a mixture of concentrated solutions of potassic monochlor acetate and nitrite:



$$2\begin{matrix} CH_2Cl \\ | \\ CO.OK \end{matrix} + 2KNO_2 + H_2O = 2KCl + K_2CO_3 + CO_2$$
$$+ 2CH_3.NO_2,$$

the nitro-methane distilling over with the water vapour. If nitro-methane be poured into an alcoholic solution of sodic hydrate, a colourless precipitate of sodium nitro-methane alcoholate:

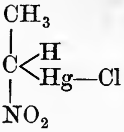
$$CH_2.NaNO_2,C_2H_6O,$$

is obtained, which by long exposure over sulphuric acid in vacuo is converted into a light white amorphous powder of sodium nitromethane, $CH_2Na.NO_2$.

Mercuric nitro-methane, probably $(NO_2)CH_2.Hg.CH_2(NO)_2$, prepared by adding mercuric chloride to the aqueous solution of sodium nitro-methane, when in the dry state, explodes with fearful violence if rubbed with a dry body.

291. *Nitro-ethane*, $CH_3.CH_2.NO_2$, is a colourless, agreeable-smelling oil, of sp. gr. 1·0582 at 13° and boiling at 113°–114°.

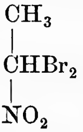
Sodium nitro-ethane, $CH_3.CHNa.NO_2$, explodes violently on heating. It deliquesces in moist air. The aqueous solution gives with mercuric chloride white needles of the formula:



$$\begin{array}{l} CH_3 \\ | \\ C<\begin{matrix} H \\ Hg—Cl \end{matrix} \\ | \\ NO_2 \end{array}$$

By treatment of a solution of sodium nitro-ethane with bromine, an oil is obtained which is a mixture of

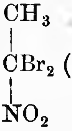
brom-nitro-ethane,



$$\begin{array}{l} CH_3 \\ | \\ CHBr_2 \\ | \\ NO_2 \end{array}$$

(boiling at 145°–148°); and

dibrom-nitro-ethane,



$$\begin{array}{l} CH_3 \\ | \\ CBr_2 \\ | \\ NO_2 \end{array}$$

(boiling at 162°–164°).

292. *Nitro-propane*, $CH_3.CH_2.CH_2.NO_2$, and *nitro-isopropane*, $\begin{matrix} CH_3 \\ CH_3 \end{matrix}> CH.NO_2$, are colourless mobile liquids, insoluble in water. The first boils at 125°–127°, the latter at 112°–117°. Both yield with alcoholic solution of sodic hydrate precipitates:

$$CH_3.CH_2.CHNa.NO_2 \text{ and } \begin{matrix} CH_3 \\ CH_3 \end{matrix}>CNa.NO_2,$$

which detonate at higher temperatures.

Nitro-isopentane, $\begin{matrix} CH_3 \\ CH_3 \end{matrix}>CH.CH_2.CH_2.NO_2$, boils at 150°–160°, and, as already mentioned, does not yield metallic derivatives.

PHOSPHORUS COMPOUNDS OF THE ALCOHOL RADICALS.

293. Similarly to the derivation of the amines from ammonia, phosphoretted hydrogen, PH_3, yields alkylic phosphine bases.

These latter show the property of uniting with acids only in a very diminished degree, the power of uniting with acids decreasing with increased replacement of hydrogen by alcohol radicals. The bodies belonging hereto form the following groups:

Primary phosphines, $P(C_nH_{2n+1})H_2$, corresponding to $N(C_nH_{2n+1})H_2$.
Secondary „ $P(C_nH_{2n+1})_2H$ „ „ $N(C_nH_{2n+1})_2H$.
Tertiary „ $P(C_nH_{2n+1})_3$ „ „ $N(C_nH_{2n+1})_3$.
Quaternary phosphonium compounds, $P(C_nH_{2n+1})_4X$, corresponding to $N(C_nH_{2n+1})_4X$.

The trivalent phosphorus compounds are distinguished from the corresponding ammonia derivatives by their ready oxidisability, absorbing oxygen by mere exposure to air, often with spontaneous inflammation. The tertiary phosphines yield oxides of the formula $P(C_nH_{2n+1})_3O$; the primary and secondary phosphines oxidising to phosphinic acids, $P(C_nH_{2n+1})_2O.OH$ and $P(C_nH_{2n+1})O(OH)_2$.

THE ALKYLIC PHOSPHINES.

294. Whilst by action of ammonia on alkylic iodides the main products of the reaction are primary amines, by passing PH_3 into heated alkylic iodides no primary or secondary phosphines are formed, but only tertiary and quaternary phosphonium iodides.

The result is just the same in the reaction between phosphonic iodide, (PH_4I), and alkylic iodides. In order to obtain the primary and secondary phosphines, the reaction between the two last-mentioned bodies must take place in presence of zincic oxide.

In order to prepare these bodies, two molecules of phosphonic iodide, one molecule of zincic oxide, and two molecules of the alkylic iodide are heated in sealed glass tubes to 150° for six to eight hours. The tube, when cold, contains a crystalline mass, which consists of the hydrides of the primary and secondary phosphines in union with zincic iodide. The reactions are expressed by the following equations:

$$ZnO + 2PH_4I + 2C_nH_{2n+1}I = ZnI_2 + 2P(C_nH_{2n+1})H_3I + OH_2,$$

and

$$ZnO + PH_4I + 2C_nH_{2n+1}I = ZnI_2 + P(C_nH_{2n+1})_2H_2I + OH_2.$$

From this mixture the primary and secondary phosphine can be readily separated from one another, and obtained in the pure state by means of the decomposition of the primary phosphonic salt by water:

$$P(C_nH_{2n+1})H_3I + xH_2O = (HI + xH_2O) + P(C_nH_{2n+1})H_2,$$

in similar manner to:

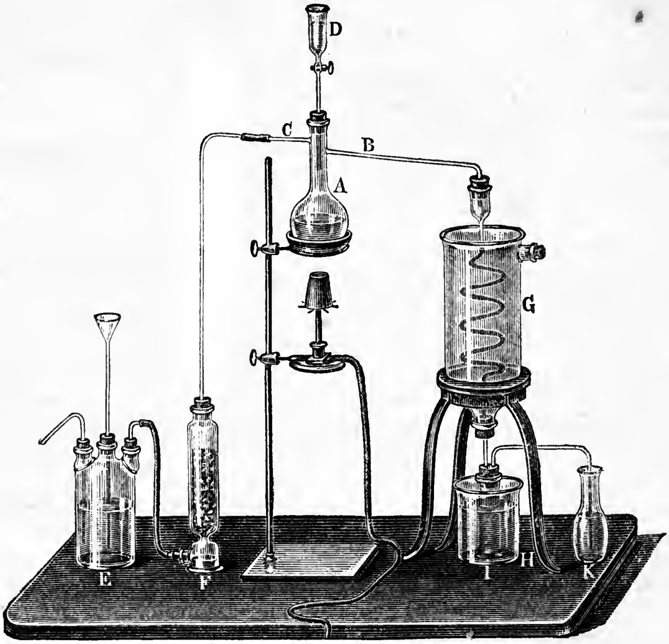
$$PH_4I + xH_2O = (HI + xH_2O) + PH_3.$$

The secondary phosphonic salts are not altered by water, but are decomposed by alkaline hydrates.

In consequence of the spontaneous inflammability of the phosphines the decomposition must be carried on in vessels filled with dry hydrogen.

The products from several tubes are for this purpose placed in a flask A standing on a sand bath (fig. 18). The flask is provided with two tubes fixed into its neck, of which the under B, bent slightly downwards, serves to carry the products of distillation to the condenser G, which contains water or a freezing mixture, the upper tube C to introduce the hydrogen, that has been generated in E and dried by passing over pumice stone moistened with sulphuric acid in F. The lower end of the condenser tube is fitted into a cylinder I which serves to collect the phosphine that passes over, and which can be surrounded by a freezing mixture. Any uncondensed phosphine vapour passes into the flask K, which contains concentrated hydriodic acid. This absorbs every trace of phosphine vapour, with separation of the crystalline phosphine hydriodide. As soon as the whole apparatus is filled with hydrogen, water free from air is allowed to flow through the tap funnel D on to the mixed iodides. The primary phosphonic iodide decomposes, with evolution of much heat, into aqueous hydriodic acid and primary phosphine, which passes, in vapour, through B, is condensed, and collects in I. During the whole process a slow stream of hydrogen passes through the apparatus. As soon as all the primary phosphine has been removed from the decomposition flask the cylinder I is changed, an excess of concentrated solution of potassic hydrate run in through the tap funnel, and the liberated secondary phosphine distilled over.

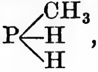
FIG. 18.



The phosphines so obtained are separated mechanically from the accompanying water, then placed with quick-lime in an apparatus similar to the above, only containing a thermometer instead of a tap funnel, and, after being completely dried by the lime, are distilled over in a state of purity. So far as yet known they are mostly strongly refractive liquids.

Primary Phosphines.

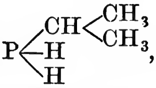
295. The primary phosphines are distinguished by their fearful odour, which resembles that of the isocyanides (§ 278). Their salts are very unstable, are decomposed by water throughout by strong acids, and, with exception of the hydro-iodides and platino-chlorides, are scarcely known. Exposed to air, the primary phosphines oxidise readily, with rise of temperature and formation of fumes, often inflaming spontaneously. They unite directly with sulphur and carbonic disulphide, forming liquid compounds.

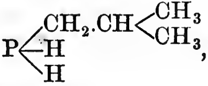
Methyl phosphine,  $P\!\left\langle\begin{matrix}CH_3\\H\\H\end{matrix}\right.$, is a colourless gas, which at −20° or by a pressure of two and a half atmospheres condenses to a mobile liquid, whose boiling point is below −14°. By cold ethylic alcohol the gas is pretty readily absorbed (1 cc. of 95 % alcohol dissolving about 20 cc. of the gas at 0°). On mixing methyl phosphine and dry hydrochloric acid gases they unite to form

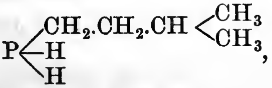
Methyl phosphonic chloride, $P(CH_3)H_3Cl$, in four-sided plates, which are very volatile and dissolve readily in concentrated hydrochloric acid. With platinic chloride this solution yields orange-coloured crystals of the formula $[P(CH_3)H_3Cl]_2PtCl_4$.

Methyl phosphonic iodide separates in thin tables or plates on passing methyl phosphine gas into concentrated hydriodic acid.

Ethyl phosphine, $P(C_2H_5)H_2$, is a mobile, colourless liquid, lighter than water, of neutral reaction, and of boiling point 25°. Its vapour bleaches cork and is largely absorbed by caoutchouc, which thereby becomes transparent and looses its elasticity. Ethyl phosphine takes fire on contact with chlorine, bromine, or concentrated nitric acid. *Ethyl phosphonic platino-chloride,* $[P(C_2H_5)H_3.Cl]_2PtCl_4$, crystallises in beautiful carmine red needles. *Ethyl phosphonic iodide* forms colourless, four-sided tables, which heated in a stream of hydrogen sublime at 100°.

Isopropyl phosphine,  $P\!\left\langle\begin{matrix}CH\!\left\langle\begin{matrix}CH_3\\CH_3\end{matrix}\right.\\H\\H\end{matrix}\right.$, boils at 41°. The liquid inflames spontaneously on exposure to air.

Isobutyl phosphine,  $P\!\left\langle\begin{matrix}CH_2.CH\!\left\langle\begin{matrix}CH_3\\CH_3\end{matrix}\right.\\H\\H\end{matrix}\right.$, a colourless liquid, boils at 62° and is lighter than water.

Isoamyl phosphine,  $P\!\left\langle\begin{matrix}CH_2.CH_2.CH\!\left\langle\begin{matrix}CH_3\\CH_3\end{matrix}\right.\\H\\H\end{matrix}\right.$, similar to the last, boiling point 106°–107°.

Secondary Phosphines.

296. The known secondary phosphines are colourless, specifically light liquids, of penetrating odour, which on exposure to air oxidise energetically, generally taking fire. With sulphur and carbonic disulphide they unite, forming liquids. Their salts are not decomposed by water, but in consequence of their great solubility are mostly difficult to crystallise with the exception of the hydriodides.

Dimethyl phosphine, $P.(CH_3)_2H$, boils at 25° (as does the metameric ethyl-phosphine). It takes fire on exposure to air. The platinochloride, $[P(CH_3)_2H_2Cl]_2PtCl_4$, is crystalline.

Diethyl phosphine, $P(C_2H_5)_2H$, is a light, spontaneously inflammable liquid of boiling point 85°. $[P(C_2H_5)_2H_2Cl]_2PtCl_4$ crystallises in large orange yellow prisms.

Diisopropyl phosphine, $P(C_3H_7)_2H$, boils at 118° and takes fire on exposure to air.

Methyl-isopropyl phosphine, $N.CH_3.C_3H_7.H$, is obtained from its hydriodide (formed directly from isopropyl phosphine and methylic iodide) as a spontaneously inflammable liquid which boils at 78°–80°.

Diisobutyl phosphine, $P(C_4H_9)_2H$, boils at 153°.

Diisoamyl phosphine, $P(C_5H_{11})_2H$, boils at 210°–215°. It is not spontaneously inflammable, but oxidises on exposure to air, forming white fumes.

Tertiary Phosphines.

297. The tertiary phosphines can be prepared by various methods, of which several have already been mentioned. Their hydriodides are formed, together with quaternary phosphonic iodides, by heating phosphonic iodide with alkylic iodides in sealed glass tubes at 160°–180°:

$$PH_4I + 3C_nH_{2n+1}I = P(C_nH_{2n+1})_3HI + 3HI,$$

and

$$PH_4I + 4C_nH_{2n+1}I = P(C_nH_{2n+1})_4I + 4HI;$$

at the same temperature also from phosphonic iodide and alcohols:

$$PH_4I + 3C_nH_{2n+1}.OH = P(C_nH_{2n+1})_3HI + 3H_2O,$$

and

$$PH_4I + 4C_nH_{2n+1}.OH = P(C_nH_{2n+1})_4I + 4H_2O;$$

and by absorption of gaseous phosphoretted hydrogen by heated alcoholic iodides:

$$PH_3 + 3C_nH_{2n+1}I = P(C_nH_{2n+1})_3HI + 2HI, \text{ \&c.}$$

If the products of these reactions be heated with potassic hydrate solution, the tertiary phosphine separates as a liquid floating on the aqueous solution:

$$P(C_nH_{2n+1})_3HI + KOH = P(C_nH_{2n+1})_3 + KI + H_2O,$$

whilst the quaternary phosphonic salts are not attacked by the alkali.

Tertiary phosphines are also prepared by heating phosphorus with alkylic iodides to 160° and afterwards heating the resulting product with the respective alcohols to the same temperature.

They are readily obtained by mixing the zinc compounds of the alcohol radicals with phosphorous trichloride in vessels filled with carbonic anhydride. As the reaction is very violent, the zinc compound must be diluted with ether, and the phosphorous chloride slowly dropped in:

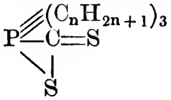
$$3Zn(C_nH_{2n+1})_2 + 2PCl_3 = 2P(C_nH_{2n+1})_3 + 3ZnCl_2.$$

The tertiary amine is not, however, in the free state, but united with the zincic chloride; on evaporating the ether, and heating the residue with potassic hydrate, the tertiary phosphine is obtained as a layer floating on the aqueous liquid. It is separated mechanically from the latter, dried by fused potassic hydrate, and rectified in a current of hydrogen.

The known tertiary phosphines are liquids insoluble in water, but miscible with alcohol and ether; they eagerly absorb an atom of oxygen from the air, and frequently take fire.

They similarly and with much evolution of heat unite with one atom of sulphur, $P(C_nH_{2n+1})_3S$, or two atoms of a halogen, $P(C_nH_{2n+1})_3Cl_2$. The latter compounds are all crystalline.

The most characteristic reaction for tertiary phosphines is their behaviour towards carbonic sulphide. If the latter be mixed with a tertiary phosphine, which, to moderate the violence of the action, has been diluted with several times its volume of ether, they both combine, with considerable evolution of heat, to compounds of the formula $P(C_nH_{2n+1})_3CS_2$, which on evaporation of the solvent are obtained in red crystals. These bodies appear to have the composition:



Water converts them into carbonic disulphide, tertiary phosphines, oxides, sulphides, &c.

The salts of the tertiary phosphines not being decomposed by water, can be prepared by means of aqueous acids, and are mostly readily soluble.

298. *Trimethyl phosphine*, $P(CH_3)_3$, is a colourless, mobile, extremely unpleasant smelling liquid, slightly denser than water. It boils at 40°–42° and inflames spontaneously in the air.

Triethyl phosphine, $P(C_2H_5)_3$, has sp. gr. ·812 at 15°, and boils at 127·5°. The odour is benumbing, but when much diluted with air resembles that of hyacinths. The hydro-acid compound can be readily obtained in crystals.

Triethyl phosphonic chloride, $P(C_2H_5)_3HCl$, gives with platinic chloride a double salt of the formula $[P(C_2H_5)_3HCl]_2PtCl_4$, difficultly soluble in water, insoluble in alcohol. The carbonic disulphide compound crystallises in red plates or needles, which melt at 95°.

Triisopropyl phosphine, $P(C_3H_7)_3$; *triisobutyl phosphine*, $P(C_4H_9)_3$, boiling point 215°; and *triisoamyl phosphine*, $P(C_5H_{11})_3$, boiling point about 300°, have also been prepared.

Quaternary Phosphonium Compounds.

299. Some methods of formation of quaternary phosphonium iodides have already been given. They are most readily obtained in a state of purity by mixing tertiary phosphines with alkylic iodides, a very violent reaction and evolution of heat occurring:

$$P(C_nH_{2n+1})_3 + C_nH_{2n+1}I = P(C_nH_{2n+1})_4I,$$

or $$P(C_nH_{2n+1})_3 + C_{n'}H_{2n'+1}I = P(C_nH_{2n+1})_3(C_{n'}H_{2n'+1})I.$$

They are not decomposed by strong solutions of alkaline hydrates, but are precipitated in crystals from their aqueous solutions.

If the solution of such an iodide be shaken with freshly precipitated argentic oxide, argentic iodide separates and quaternary phosphonic hydrates are formed :

$$P(C_nH_{2n+1})_4I + AgOH = AgI + P(C_nH_{2n+1})_4OH.$$

These hydrates completely resemble the quaternary ammonic hydrates. They react strongly alkaline, have a caustic action, eagerly absorb carbonic anhydride from the air, and completely neutralise the strongest acids. They are crystallisable, but extremely soluble and deliquesce in the air. Their salts are also mostly soluble in water. The platino-chlorides crystallise in difficultly soluble octahedra.

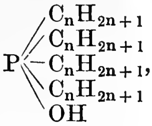
Whilst the quaternary ammonic compounds on distillation decompose into tertiary amine, water, and olefine, the phosphonium hydrates, in consequence of the strong affinity of oxygen for phosphorus, yield oxides of tertiary phosphines and the respective paraffins :

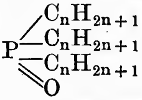
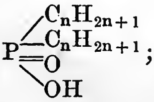
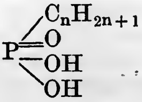
$$P(C_nH_{2n+1})_4.OH = P(C_nH_{2n+1})_3O + C_nH_{2n+2}.$$

Tetra-ethyl and tetramethyl compounds have been especially investigated; the iodides are first prepared, from these the hydrates, $P(CH_3)_4.OH$ and $P(C_2H_5)_4.OH$, and many of their salts. Iodides containing two different alcohol radicals have been prepared among others :

$$P(CH_3)_3(C_2H_5)I$$
$$P(C_2H_5)_3(C_5H_{11})I.$$

Oxides of the Phosphines.

300. These oxidation products of the tetralkyl phosphonium hydrates,  are formed directly from the latter by direct union with the atmospheric oxygen or by action of nitric acid.

The tertiary phosphines yield with atmospheric oxygen the nearly indifferent oxides ; the secondary phosphines, by oxidation with nitric acid, give the dialkylic phosphinic acids ; whilst the primary phosphines similarly yield monalkylic phosphinic acids, 

In the latter two cases, as in the first, the phosphorus atom, by uniting with an oxygen atom, becomes pentavalently saturated, but at the same time other atoms of oxygen place themselves in between the phosphorus and its directly united hydrogen, forming hydroxyl groups. The alcohol radicals, on the other hand, are so firmly united to the phosphorus that even the strongest nitric acid, at the temperature of the water bath, fails to separate them. The oxidation to phosphoric acid can only be effected at a temperature of about 200° by fuming nitric acid, the alcohol radical being then totally oxidised.

301. The oxides of the tertiary phosphines are obtained with less danger by distilling quatenary phosphonic hydrates:

$$P(C_nH_{2n+1})_4.OH = P(C_nH_{2n+1})_3O + C_nH_{2n+2},$$

and by treatment of tertiary phosphines with mercuric oxide:

$$P(C_nH_{2n+1})_3 + HgO = P(C_nH_{2n+1})_3O + Hg,$$

than by direct oxidation.

Trimethyl phosphine oxide, $P(CH_3)_3O$, forms readily soluble crystals, which deliquesce in damp air.

Triethyl phosphine oxide, $P(C_2H_5)_3O$, crystallises in very deliquescent needles. It melts on heating and boils at 240° without decomposition. Concentrated hydrochloric, hydrobromic, and hydriodic acids convert it into triethyl phosphine dichloride, $P(C_2H_5)_3Cl_2$, dibromide, $P(C_2H_5)_3Br_2$, and diiodide, $P(C_2H_5)_3I_2$, crystalline compounds which can also be obtained by moderated action of the halogens on triethyl phosphine.

Triethyl phosphine oxide gives, with strong acids, salts which are difficult to obtain pure.

Metallic sodium reduces it to triethyl phosphine.

302. The *sulphides of the tertiary phosphines,* $P(C_nH_{2n+1})_3S$, may be mentioned here. They are crystalline, and are obtained from the tertiary phosphines by direct addition of sulphur, which reacts with considerable evolution of heat.

On bringing sulphur into contact with triethyl phosphine, it melts to a globule, which floats on the liquid and slowly dissolves. When completely saturated with sulphur the liquid solidifies to a crystalline mass of triethyl phosphine sulphide, $P.(C_2H_5)_3S$, which dissolves pretty readily in boiling water, and separates on cooling in beautiful needles. It is readily soluble in alcohol and ether. It melts at 94°; by boiling with mercuric or plumbic oxide it is converted into triethyl phosphine oxide:

$$P(C_2H_5)_3S + HgO = HgS + P(C_2H_5)_3O;$$

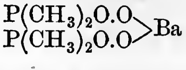
by sodium it is reduced to triethyl phosphine:

$$P(C_2H_5)_3S + Na_2 = Na_2S + P(C_2H_5)_3.$$

303. The monobasic dialkyl phosphinic acids, $P(C_nH_{2n+1})_2O.OH$, are obtained by action of concentrated nitric acid upon secondary phosphonic chlorides. The liquid heats spontaneously to boiling, and evolves chlorine and torrents of nitrous fumes. As soon as the reaction is finished, the excess of nitric acid is removed by repeated evaporation on the water bath with concentrated hydrochloric acid, the latter being finally in great part expelled. The residue is then dissolved in water and completely freed from hydrochloric acid by shaking with argentic oxide.

To obtain the free acid, the silver is removed from the filtrate by means of hydric sulphide, and after again filtering the liquid evaporated on the water bath.

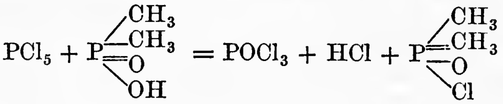
Dimethyl phosphinic acid, $P(CH_3)_2O.OH$, solidifies to a paraffin-like mass, which melts at 76° and can be volatilised unchanged. The silver salt, $P(CH_3)_2O.OAg$, prepared by saturation of the acid with argentic oxide, is extremely soluble in water, but is precipitated by strong alcohol in interlaced needles. The baric salt



$$\left.\begin{matrix}P(CH_3)_2O.O\\P(CH_3)_2O.O\end{matrix}\right>Ba$$

and the analogous plumbic salt dry to amorphous varnishes, which are readily soluble in alcohol.

By bringing together dimethyl phosphinic acid and phosphonic pentachloride there is formed, according to the equation:



$$PCl_5 + P\left\{\begin{matrix}CH_3\\CH_3\\=O\\OH\end{matrix}\right. = POCl_3 + HCl + P\left\{\begin{matrix}CH_3\\CH_3\\=O\\Cl\end{matrix}\right.$$

dimethyl oxyphosphine chloride, which distils at 204° and solidifies in crystals on cooling. It melts at 66° and is reconverted by water into the acid:

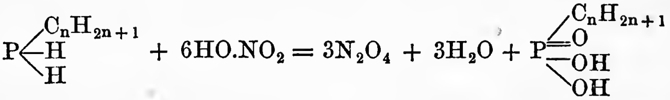
$$P(CH_3)_2O.Cl + HOH = HCl + P(CH_3)_2O.OH.$$

Diethyl phosphinic acid, $P(C_2H_5)_2O.OH$, is left on evaporation as a strongly acid liquid. The argentic salt is also precipitated by alcohol from its aqueous solutions in needles.

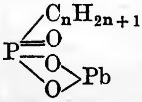
304. The dibasic monalkyl phosphinic acids:

$$P(C_nH_{2n+1})O(OH)_2,$$

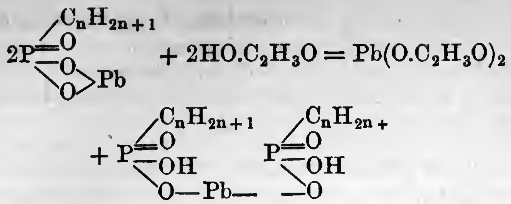
result from passing the vapours of primary phosphines into strong nitric acid:



$$P\left\{\begin{matrix}C_nH_{2n+1}\\H\\H\end{matrix}\right. + 6HO.NO_2 = 3N_2O_4 + 3H_2O + P\left\{\begin{matrix}C_nH_{2n+1}\\=O\\OH\\OH\end{matrix}\right.$$

When the violent oxidation has ceased, the liquid is evaporated several times on the water bath, so as to expel nearly all the nitric acid; the aqueous solution then boiled with plumbic oxide, plumbic nitrate remaining dissolved, whilst insoluble plumbic monalkyl phosphinate,  $P\left\{\begin{matrix}C_nH_{2n+1}\\=O\\\left.\begin{matrix}O\\O\end{matrix}\right>Pb\end{matrix}\right.$, and some plumbic phosphate separate.

The residue, after washing with water, is heated with acetic acid, which leaves the plumbic phosphate undissolved and converts the neutral monalkyl phosphinate into the soluble acid salt:



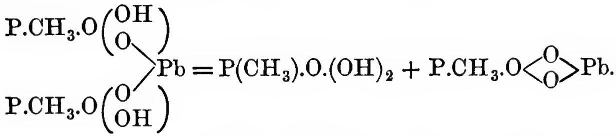
$$2P\begin{cases}C_nH_{2n+1}\\ =O\\ -O\\ -O\end{cases}\!\!>Pb + 2HO.C_2H_3O = Pb(O.C_2H_3O)_2 + P\begin{cases}C_nH_{2n+1}\\ =O\\ -OH\\ -O-Pb-\end{cases} P\begin{cases}C_nH_{2n+}\\ =O\\ -OH\\ -O\end{cases}$$

The filtrate is decomposed by sulphuretted hydrogen, and after separation of the plumbic sulphide the liquid evaporated until all acetic acid has been expelled.

Methyl phosphinic acid, $P(CH_3)O(OH)_2$, forms spermaceti-like crystals, which melt at 105°, partially volatilise unchanged, and are readily soluble in water and alcohol. The solutions react strongly acid. If the acid in presence of water be digested with carbonates, the soluble acid salts are formed; by boiling with metallic oxides or by strongly basic hydrates they are converted into neutral salts of alkaline reaction.

The salts of the alkalies are all difficultly crystallisable.

The acid baric salt $Ba\!<\!\begin{matrix}O(P.CH_3.O.OH)\\ O(P.CH_3.O.OH)\end{matrix}$ dries to a gummy mass. If a pretty concentrated solution of the salt be boiled with plumbic carbonate, and filtered hot, there separates on cooling the acid lead salt $Pb\!<\!\begin{matrix}O(P.CH_3.O.OH)\\ O(P.CH_3.O.OH)\end{matrix}$ in brilliant colourless needles, which by washing with pure water are resolved into the free acid and the insoluble, amorphous, neutral salt:

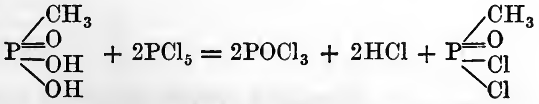


$$\left.\begin{matrix}P.CH_3.O\begin{pmatrix}OH\\ O\end{pmatrix}\\ P.CH_3.O\begin{pmatrix}O\\ OH\end{pmatrix}\end{matrix}\right>Pb = P(CH_3).O.(OH)_2 + P.CH_3.O\!<\!\begin{matrix}O\\ O\end{matrix}\!>\!Pb.$$

The acid silver salt, $P(CH_3).O\begin{pmatrix}OH\\ OAg\end{pmatrix}$, which is readily soluble in water in presence of a little free acid, and which crystallises in beautiful needles, behaves similarly with water, being decomposed with separation of the amorphous insoluble neutral silver salt:

$$P(CH_3)O(OAg)_2.$$

Phosphoric pentachloride converts methyl phosphinic acid into the dichloride of the radical $P(CH_3)O$:



$$P\begin{cases}CH_3\\ =O\\ -OH\\ -OH\end{cases} + 2PCl_5 = 2POCl_3 + 2HCl + P\begin{cases}CH_3\\ =O\\ -Cl\\ -Cl\end{cases}$$

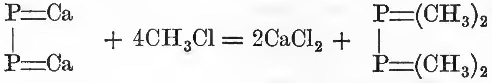
This methyl phosphinic dichloride forms dazzling white crystals, which melt at 32° and boil at 163°. Water reconverts it with explosive violence into the acid:

$$P(CH_3)OCl_2 + 2H_2O = 2HCl + 2P(CH_3)O(OH)_2.$$

Ethyl phosphinic acid, prepared from ethyl phosphine by the same method as the preceding, resembles spermaceti at ordinary temperatures, melts at 44°, and though difficult to moisten with water is largely soluble therein. Its salts correspond to those of methyl phosphinic acid.

Other Phosphorus Compounds of the Alcohol Radicals.

305. By action of methylic chloride on phosphide of calcium at high temperatures, diphosphor tetramethyl or phosphor cacodyl (compare cacodyl, § 318), $P_2(CH_3)_4$, is obtained as a thick oily liquid, which boils at 250° and inflames when exposed to air. Its formation is analogous to that of liquid phosphoretted hydrogen, P_2H_4, which it corresponds to:



$$\begin{array}{l} P{=}Ca \\ | \\ P{=}Ca \end{array} + 4CH_3Cl = 2CaCl_2 + \begin{array}{l} P{=}(CH_3)_2 \\ | \\ P{=}(CH_3)_2 \end{array}$$

As liquid phosphoretted hydrogen on contact with hydrochloric acid decomposes into the solid and gaseous

$$5P_2H_4 = 6CH_3 + P_4H_2,$$

so similarly the methyl compound decomposes into trimethyl phosphonic chloride and tetra-phosphor-dimethyl:

$$5P_2(CH_3)_4 + 6HCl = 6P(CH_3)_3HCl + P_4(CH_3)_2.$$

The latter is an amorphous, odourless, and tasteless yellow body.

ARSENIC COMPOUNDS OF THE RADICALS.

306. The compounds of arsenic with the alcohol radicals show some similarities to the nitrogen compounds. The quaternary arsonic salts derived from the strongly basic tetralkyl arsonic hydrates, $As(C_nH_{2n+1})_4.OH$, agree completely in chemical character with the corresponding ammonic compounds.

The tertiary arsines are also known; they are destitute of the distinctly basic properties which the tertiary phosphines possess, but, like these latter, they unite with one atom of oxygen or sulphur or two halogen atoms.

Compounds corresponding to the primary and secondary amines and phosphines are entirely wanting in the arsenic compounds, but compounds of one atom of arsenic united with two alcohol radicals form the mono- or trivalent radical of the so-called cacodyl derivatives, where they are in union with negative elements:

$$As(C_nH_{2n+1})_2Cl \text{ and } As(C_nH_{2n+1})_2Cl_3.$$

In similar manner one alcohol radical united to arsenic appears as a divalent or quadravalent radical:

$$As(C_nH_{2n+1})Cl_2 \text{ and } As(C_nH_{2n+1})Cl_4.$$

307. The compounds in which arsenic is triad, such as

$$As(C_nH_{2n+1})_3, As(C_nH_{2n+1})_2Cl, \text{ and } As(C_nH_{2n+1})Cl_2,$$

are mostly volatile without decomposition; those in which it is pentad, such as $As(C_nH_{2n+1})_4Cl$, $As(C_nH_{2n+1})_3Cl_2$, $As(C_nH_{2n+1})_2Cl_3$, and $As(C_nH_{2n+1})Cl_4$, decompose at more or less high temperature, losing one halogen atom and one alcohol radical. This decomposition occurs especially readily with the halogen compounds, and the temperature of decomposition is the lower the fewer alcohol radicals and the more halogen atoms the molecule contains. The alkyl arsenic compounds can therefore, by a series of manipulations, be converted into trivalent inorganic arsenic compounds. Such a series of changes is the following :

$$As(C_nH_{2n+1})_4Cl \text{ by heating} = As(C_nH_{2n+1})_3 + C_nH_{2n+1}Cl$$
$$As(C_nH_{2n+1})_3 + Cl_2 \text{ at ord. temperatures} = As(C_nH_{2n+1})_3Cl_2$$
$$As(C_nH_{2n+1})_3Cl_2 \text{ by heating} = As(C_nH_{2n+1})_2Cl + C_nH_{2n+1}Cl$$
$$As(C_nH_{2n+1})_2Cl + Cl_2 \text{ in the cold} = As(C_nH_{2n+1})_2Cl_3$$
$$As(C_nH_{2n+1})_2Cl_3 \text{ at } 40^\circ\text{–}50^\circ = As(C_nH_{2n+1})Cl_2 + C_nH_{2n+1}Cl$$
$$As(C_nH_{2n+1})Cl_2 + Cl_2 \text{ in a freezing mixture} = As(C_nH_{2n+1})Cl_4$$
$$As(C_nH_{2n+1})Cl_4 \text{ even at } 0^\circ = AsCl_3 + C_nH_{2n+1}Cl.$$

All alkyl arsenic compounds—especially the volatile ones—are in the highest degree poisonous, so that their preparation and investigation require extraordinary precautions.

Quaternary Arsonium Compounds.

308. By heating alkylic iodides with sodic or zincic arsenide in apparatus filled with dry carbonic anhydride violent reaction occurs, by which partly cacodyls, $As_2(C_nH_{2n+1})_4$, but in larger proportion tertiary arsines, $As(C_nH_{2n+1})_3$, are formed. If the alkylic iodide be employed in excess it forms crystalline quaternary arsonic iodides, according to the equation :

$$AsNa_3 + 4C_nH_{2n+1}I = 3NaI + As(C_nH_{2n+1})_4I.$$

These latter are only separated from the sodic iodide with difficulty; it is more usual, therefore, to avoid excess of the iodide, and to purify the more volatile tertiary arsine from the cacodyl by fractional distillation. It is then mixed with the alkylic iodide, and soon yields at ordinary temperature the arsonic iodide :

$$As(C_nH_{2n+1})_3 + C_nH_{2n+1}I = As(C_nH_{2n+1})_4I,$$

from which, by shaking its aqueous solution with freshly precipitated argentic oxide, the quaternary arsonic hydrate is obtained :

$$As(C_nH_{2n+1})_4I + AgOH = AgI + As(C_nH_{2n+1})_4OH.$$

Mixed quaternary arsonic iodides can be obtained from tertiary arsines and the iodide of another alcohol radical :

$$As(C_nH_{2n+1})_3 + C_{n'}H_{2n'+1}I = As(C_nH_{2n+1})_3(C_{n'}H_{2n'+1})I;$$

a further group by heating the cacodyls with the iodides of other alcohol radicals :

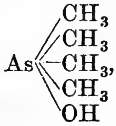
$$As_2(C_nH_{2n+1})_4 + 2(C_{n'}H_{2n'+1})I = As(C_nH_{2n+1})_2I \\ + As(C_nH_{2n+1})_2(C_{n'}H_{2n'+1})_2I.$$

The quaternary arsonic hydrates are crystallisable, very easily soluble compounds, which react strongly alkaline, precipitate metallic hydrates from their salts, liberate ammonia from ammonic salts, absorb carbonic anhydride from the air, and unite with acids to form salts. The latter are easily prepared by the decomposition of the iodides with soluble silver salts.

309. *Tetramethyl arsonic iodide*, $As(CH_3)_4I$, forms colourless shining plates or prisms, whose hot saturated aqueous solution dissolves much iodine, and on cooling yields brown metallic-looking needles of *tetramethyl arsonic periodide*, $As(CH_3)_4I_3$. Combined with arsenious iodide, tetramethyl arsonic iodide is obtained by heating powdered arsenic with twice its weight of methylic iodide in sealed tubes at 160°–175° :

$$As_2 + 4CH_3I = As(CH_3)_4I,AsI_3.$$

The compound crystallised from hot water forms orange yellow tables, which with solution of potassic hydrate give tetramethyl arsonic iodide, potassic iodide, and potassic arsenite, or by distillation with solid potassic hydrate gives off trimethyl arsine.

Tetramethyl arsonic hydrate, $As(CH_3)_4.OH$ =  $As\begin{cases}CH_3\\CH_3\\CH_3\\CH_3\\OH\end{cases}$, crystallises in deliquescent, strongly alkaline tables. Its salts are very hygroscopic.

310. By action of tetramethyl arsonic iodide upon zinc methyl in an atmosphere of carbonic anhydride, arsenic pentamethylide, $As(CH_3)_5$, is obtained as a difficultly volatile liquid :

$$2As(CH_3)_4I + Zn(CH_3)_2 = ZnI_2 + 2As(CH_3)_5.$$

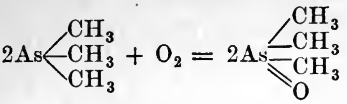
311. *Tetrethyl arsonic iodide*, $As(C_2H_5)_4I$, crystallises in colourless needles, readily soluble in alcohol and water, insoluble in ether, and gives with iodine and arsenious iodide compounds exactly analogous to those of tetramethyl arsonic iodide. *Tetrethyl arsonic hydrate* is a deliquescent, strongly alkaline white mass, which gives with hydrochloric acid the deliquescent crystalline *tetrethyl arsonic chloride* $As(C_2H_5)_4Cl,4H_2O$. If the solution of the latter be mixed with platinic chloride, orange red crystals slowly separate, difficultly soluble in cold water, of the double salt $[As(C_2H_5)_4Cl]_2PtCl_4$.

312. The best known mixed arsonic derivatives are those of *dimethyl-diethyl arsonium* : the iodide, $As(CH_3)_2(C_2H_5)_2I$; the chloride, which crystallises in long needles; the platino-chloride, $[As(CH_3)_2(C_2H_5)_2Cl]_2PtCl_4$, in orange red prisms; the nitrate, $As(CH_3)_2(C_2H_5)_2.O.NO_2$, in deliquescent granules; and the sulphate, $[As(CH_3)_2(C_2H_5)_2]_2SO_4$, in readily soluble octahedra.

Tertiary Arsines, $As(C_nH_{2n+1})_3$.

313. The preparation of tertiary arsines from sodic arsenide and alcoholic iodides has been already given (§ 308), as also their formation by the dry distillation of quaternary arsonic compounds, more particularly in the presence of solid alkaline hydrates. The tertiary arsines known are distillable liquids insoluble in water and of most unpleasant odour. They eagerly absorb oxygen from the air, with considerable evolution of heat. They also unite with sulphur and the halogens, in the last case always with two atoms.

314. *Trimethyl arsine,* $As(CH_3)_3$, is a colourless mobile liquid, boiling below 100°. Trimethyl arsine oxide, $As(CH_3)_3O$, resulting on exposure to air, according to the equation :



$$2As\begin{cases}CH_3\\CH_3\\CH_3\end{cases} + O_2 = 2As\begin{cases}CH_3\\CH_3\\CH_3\\O\end{cases}$$

forms beautiful crystals, which are very deliquescent. The sulphide, $As(CH_3)_3S$, and the halogen compounds, $As(CH_3)_3I_2$, $As(CH_3)_3Br$, and $As(CH_3)_3Cl_2$, are crystalline hygroscopic bodies.

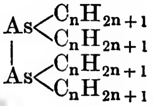
315. *Triethyl arsine,* $As(C_2H_5)_3$, is also a colourless liquid, not miscible with water. At 140° it begins to distil, with slight decomposition and separation of metallic arsenic. It fumes in the air without taking fire, and is converted into triethyl arsine oxide, $As(C_2H_5)_3O$, a heavy, unpleasant-smelling yellowish oil.

If an ethereal solution of triethyl arsine be boiled with flowers of sulphur, and the ether evaporated from the filtered liquid, *triethyl arsine sulphide,* $As(C_2H_5)_3S$, crystallises in fine odourless prisms, soluble in water, alcohol, and ether, and melting at slightly above 100°.

By addition of an ethereal solution of iodine to one of triethyl arsine, triethyl arsine diiodide, $As(C_2H_5)_3I_2$, separates as a sulphur yellow flocculent precipitate, readily soluble in alcohol and ether and deliquescing in air to a dark syrup. Triethyl arsine dibromide, $As(C_2H_5)_3Br_2$, prepared similarly to the iodide, forms a pale yellow crystalline mass, which is soluble in ether and is very deliquescent.

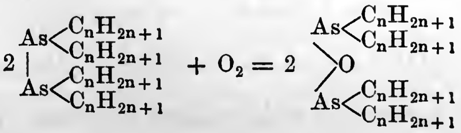
Dialkylarsenic Compounds.

316. The compounds of arsenic with two alcohol radicals do not occur isolated, but in molecules containing two such groups united together by the third valence of the arsenic :



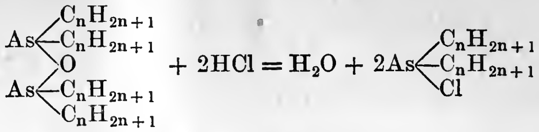
$$\begin{array}{l}As\begin{cases}C_nH_{2n+1}\\C_nH_{2n+1}\end{cases}\\ \vert\\ As\begin{cases}C_nH_{2n+1}\\C_nH_{2n+1}\end{cases}\end{array}$$

These bodies, corresponding to diphosphor tetramethyl (§ 305), are known as cacodyls (from κακός, bad, and ὄζειν, to smell). On exposure to air they oxidise with great energy, and inflame in consequence of the increase of temperature so caused. If the action of the atmospheric oxygen be moderated the cacodyl oxides are obtained :



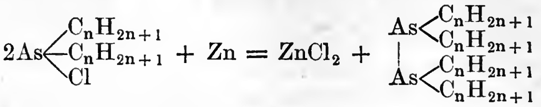
$$2\begin{array}{l}As\begin{cases}C_nH_{2n+1}\\C_nH_{2n+1}\end{cases}\\ \vert\\ As\begin{cases}C_nH_{2n+1}\\C_nH_{2n+1}\end{cases}\end{array} + O_2 = 2\begin{array}{l}As\begin{cases}C_nH_{2n+1}\\C_nH_{2n+1}\end{cases}\\ \quad\rangle O\\ As\begin{cases}C_nH_{2n+1}\\C_nH_{2n+1}\end{cases}\end{array}$$

from which, by action of the hydro-acids, the corresponding halogen compounds can be prepared :



$$\begin{array}{l}\mathrm{As}\left<\begin{array}{l}C_nH_{2n+1}\\ C_nH_{2n+1}\end{array}\right.\\ \quad\; O\\ \mathrm{As}\left<\begin{array}{l}C_nH_{2n+1}\\ C_nH_{2n+1}\end{array}\right.\end{array} + 2HCl = H_2O + 2\mathrm{As}\left<\begin{array}{l}C_nH_{2n+1}\\ C_nH_{2n+1}\\ Cl\end{array}\right.$$

These latter by action of zinc filings are reconverted into cacodyl :



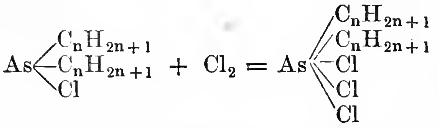
$$2\mathrm{As}\left<\begin{array}{l}C_nH_{2n+1}\\ C_nH_{2n+1}\\ Cl\end{array}\right. + Zn = ZnCl_2 + \begin{array}{l}\mathrm{As}\left<\begin{array}{l}C_nH_{2n+1}\\ C_nH_{2n+1}\end{array}\right.\\ \;|\\ \mathrm{As}\left<\begin{array}{l}C_nH_{2n+1}\\ C_nH_{2n+1}\end{array}\right.\end{array}$$

The halogen compounds can also be prepared by the direct action of the free halogens on the cacodyls:

$$[As(C_nH_{2n+1})_2]_2 + I_2 = 2As(C_nH_{2n+1})_2I.$$

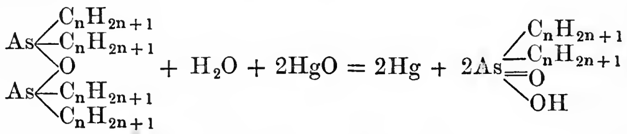
When brought into contact with sulphur they are converted directly into sulphides of analogous composition to the oxides.

317. In addition to the above compounds which contain the arsenic in the trivalent state, cacodylic compounds are also known in which the arsenic is pentavalent, and which are obtained from the preceding by direct addition of negative elements. For instance, the haloid compounds unite at ordinary temperatures with two more halogen atoms :



$$\mathrm{As}\left<\begin{array}{l}C_nH_{2n+1}\\ C_nH_{2n+1}\\ Cl\end{array}\right. + Cl_2 = \mathrm{As}\left<\begin{array}{l}C_nH_{2n+1}\\ C_nH_{2n+1}\\ Cl\\ Cl\\ Cl\end{array}\right.$$

The oxides reduce the oxygen compounds of the noble metals when suspended in water, being converted into monobasic acids, *cacodylic acids,* which correspond in composition to the monobasic phosphinic acids (§ 303) :



$$\begin{array}{l}\mathrm{As}\left<\begin{array}{l}C_nH_{2n+1}\\ C_nH_{2n+1}\end{array}\right.\\ \quad\; O\\ \mathrm{As}\left<\begin{array}{l}C_nH_{2n+1}\\ C_nH_{2n+1}\end{array}\right.\end{array} + H_2O + 2HgO = 2Hg + 2\mathrm{As}\left<\begin{array}{l}C_nH_{2n+1}\\ C_nH_{2n+1}\\ =O\\ OH\end{array}\right.$$

318. The dimethyl arsenic compounds are best known.

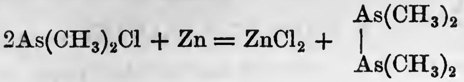
Diarsentetramethyl, methyl cacodyl, or shortly *cacodyl :*

$$As_2(CH_3)_4 = \begin{array}{l}As(CH_3)_2\\ \;|\\ As(CH_3)_2\end{array}.$$

is formed in small quantity, together with trimethyl-arsine, by the action of methylic iodide upon sodic arsenide, and can be separated therefrom by fractional distillation.

It is more usual to prepare it by the action of metals, especially of zinc, upon cacodylic chloride.

Cacodylic chloride is placed, together with zinc turnings, into vessels filled with carbonic anhydride, and heated gently on the water bath until the reaction is completed :



$$2As(CH_3)_2Cl + Zn = ZnCl_2 + \begin{array}{l}As(CH_3)_2\\ |\\ As(CH_3)_2\end{array}$$

After cooling the zincic chloride is dissolved by addition of water, whilst the free cacodyl collects at the bottom as a heavy oily layer; this is separated mechanically from the zincic chloride solution, dried by means of calcic chloride, and obtained pure by distillation in an atmosphere of carbonic anhydride.

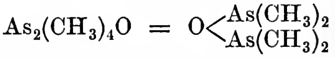
Cacodyl so obtained is a clear, colourless, strongly refractive liquid, which boils at about 170° and solidifies to an ice-like mass at $-6°$. On coming into contact with atmospheric air it inflames and burns with a livid flame:

$$2As_2(CH_3)_4 + 17O_2 = 2As_2O_3 + 8CO_2 + 12H_2O.$$

By heating to 300°–400° it decomposes completely into metallic arsenic and a mixture of methane and ethylene.

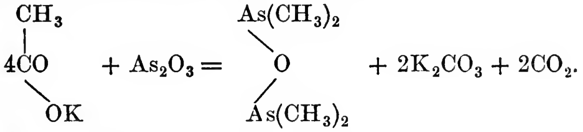
$$As_2(CH_3)_4 = 2CH_4 + C_2H_4 + As_2.$$

319. *Dimethyl-arsen oxide*, or *cacodylic oxide :*

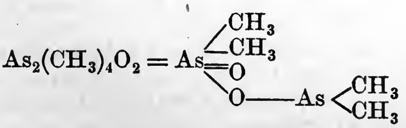


$$As_2(CH_3)_4O = O\begin{array}{l}As(CH_3)_2\\ As(CH_3)_2\end{array}$$

In an impure state this body (formerly called *alkarsin*) is obtained by the distillation of potassic acetate with arsenious oxide:



The liquid which comes over, on account of its poisonous nature and ready inflammability, must be collected in well-cooled and carefully closed vessels under water, and later, after mechanical separation of the water, be distilled from baric oxide in vessels filled with dry carbonic anhydride. Obtained anhydrous in this way, cacodylic oxide forms a colourless, strongly refractive liquid, of fearful odour, whose vapour causes nausea and vomiting. Its sp. gr. is 1·462; it solidifies at $-25°$ to silky scaly crystals; its boiling point is 150°. It is insoluble in water, but miscible with alcohol and ether. The property of spontaneous inflammability in air of this preparation is due to a small admixture of cacodyl. When mixed with a little water, purified alkarsin slowly absorbs oxygen from the air, and is converted into a syrupy solution of cacodylic cacodylate:



which on distillation is decomposed into pure cacodylic oxide, which passes over with the aqueous vapour, and cacodylic acid, which remains behind:

$$2As_2(CH_3)_4O_2 + H_2O = 2As(CH_3)_2O.OH + As_2(CH_3)_4O.$$

Cacodylic oxide so prepared has all the properties of purified alkarsin, except that it is not spontaneously inflammable on exposure to air; it oxidises, however, slowly first to cacodylic cacodylate and finally to cacodylic acid.

Cacodylic oxide combines with mineral acids, forming salts which are mostly difficultly crystallisable. Of these cacodylic sulphate is most easily prepared, by solution of cacodylic oxide in warm dilute sulphuric acid. On cooling the liquid fine needles of

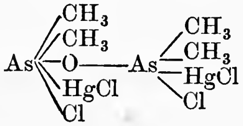
$$\left.\begin{array}{l}As(CH_3)_2.O\\As(CH_3)_2.O\end{array}\right>SO_2\ (?)$$

separate.

A dilute alcoholic solution of cacodylic oxide is precipitated by alcoholic mercuric chloride as a voluminous white precipitate. This contains calomel, but also a compound of the formula

$$As_2(CH_3)_4O,2HgCl_2,$$

probably



which is soluble in hot water and crystallises in nacreous scales or rhombic tables.

320. *Monohaloid Compounds of Cacodyl.—Dimethyl-arsen chloride,* or *cacodylic chloride,* $As(CH_3)_2Cl$, is obtained by passing dry hydrochloric acid gas into crude cacodylic oxide, and subsequently rectifying the product over calcic chloride and magnesia. It is obtained purer by distillation of the above-mentioned cacodylic oxide-mercuri-chloride with hydrochloric acid. It is a colourless liquid of stupefying odour. The boiling point is about 100°.

Platinic chloride gives with a hydrochloric solution of cacodylic chloride a red insoluble pulverulent precipitate of

$$[As(CH_3)_2Cl]_2,PtCl_4.$$

Dimethyl-arsen bromide, or *cacodylic bromide,* $As(CH_3)_2Br$, is obtained from cacodylic oxide-mercuri-chloride, by distillation with concentrated hydrobromic acid, as a liquid resembling the chloride.

Dimethyl-arsen iodide, cacodylic iodide, obtained from alkarsin by distillation with concentrated hydriodic acid, and purified by distillation from quick-lime and from calcic chloride, is a yellowish liquid, boiling much above 100°.

By action of water upon the monohaloid derivatives of cacodyl one quarter of the halogen is withdrawn, and the so-called cacodylic oxyhaloids are formed, of which $As_8(CH_3)_{16}Cl_6O$ and $As_8(CH_3)_{16}Br_6O$ are liquids fuming on exposure to air, whilst $As_8(CH_3)_{16}I_6O$ is a yellow crystalline mass. All three can be distilled apparently unchanged, but in reality are decomposed into cacodylic oxide and haloid, which recombine on cooling.

321. *Cacodylic cyanide,* $As(CH_3)_2.CN$, crystallises in large prisms of diamond lustre, of melting point 37° and boiling point 140°. This extremely poisonous body is obtained by distillation of alkarsin with concentrated hydrocyanic acid or of cacodylic chloride with mercuric cyanide.

322. *Dimethyl-arsen trichloride, cacodylic trichloride,* $As(CH_3)_2Cl_3$, results from the action of chlorine gas upon cacodylic chloride, the latter being previously diluted with carbonic disulphide in order to moderate the violence of the reaction. The trichloride separates partially in crystalline plates. Another method of preparation consists in the action of phosphoric chloride on cacodylic acid, placed under anhydrous ether:

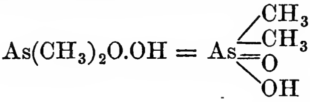
$$As(CH_3)_2O.OH + 2PCl_5 = As(CH_3)_2Cl_3 + HCl + 2POCl_3.$$

It is dissolved by ether or carbonic disulphide, and crystallises on evaporation of these solutions in clear plates. It decomposes at 40°–50° into arsen-monomethyl dichloride and methylic chloride:

$$As(CH_3)_2Cl_3 = As(CH_3)Cl_2 + CH_3Cl.$$

By water it is readily converted into cacodylic chloro-dihydrate (§ 324).

323. *Cacodylic acid, dimethyl arsinic acid:*



$$As(CH_3)_2O.OH = As\begin{cases}CH_3\\CH_3\\=O\\OH\end{cases}$$

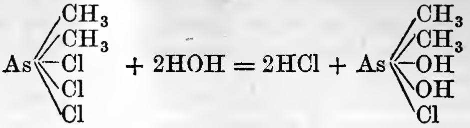
Cacodylic acid is usually prepared by means of cacodylic oxide and mercuric oxide. For this purpose alkarsin is added to several times its volume of water, and mercuric oxide slowly added with gentle shaking until the odour of alkarsin has completely disappeared:

$$[As(CH_3)_2]_2O + 2HgO + H_2O = 2Hg + 2As(CH_3)_2.O.OH.$$

The liquid poured off the reduced mercury contains cacodylic acid and some mercuric cacodylate, for whose complete decomposition a small quantity more alkarsin is added. By evaporation of the clear solution cacodylic acid is obtained in large colourless prisms, which melt at 200°, with partial decomposition. It is readily soluble in water, difficultly in alcohol, insoluble in ether. The solution reacts and tastes decidedly acid. By reducing agents it is reconverted into cacodylic oxide. Oxidising agents, even fuming nitric acid, are without action on it.

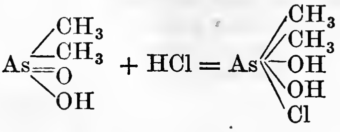
It reacts on metallic oxides and carbonates, forming crystalline salts, cacodylates, soluble in water. *Potassic cacodylate* forms concentricly grouped needles, which quickly deliquesce in moist air; *argentic cacodylate,* $As(CH_3)_2O.OAg$, crystallises in delicate colourless needles, which blacken on exposure to light; *cacodylic cacodylate* has been already mentioned (§ 319).

324. *Cacodylic chloro-dihydrate,* or *cacodylic acid hydrochloride,* is obtained from cacodylic trichloride by action of water, or more readily by dissolving cacodylic acid in concentrated hydrochloric acid and evaporation of the liquid in vacuo. It separates in deliquescent, acid-reacting leafy crystals, of the formula $As(CH_3)_2O_2H_2Cl$. Its formation is expressed by the following equations:



$$\mathrm{As}\left\langle\begin{array}{l}CH_3\\CH_3\\Cl\\Cl\\Cl\end{array}\right. + 2HOH = 2HCl + \mathrm{As}\left\langle\begin{array}{l}CH_3\\CH_3\\OH\\OH\\Cl\end{array}\right.$$

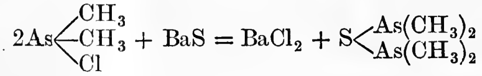
and



$$\mathrm{As}\left\langle\begin{array}{l}CH_3\\CH_3\\=O\\OH\end{array}\right. + HCl = \mathrm{As}\left\langle\begin{array}{l}CH_3\\CH_3\\OH\\OH\\Cl\end{array}\right.$$

325. *Sulphides of Cacodyl.*—Two compounds of cacodyl with sulphur are known.

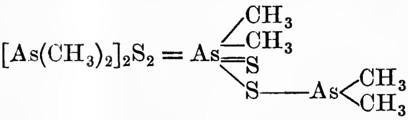
Cacodylic sulphide, $[As(CH_3)_2]_2S$, corresponds in composition to cacodylic oxide. It is obtained by distillation of cacodylic chloride with baric sulphide:



$$2\mathrm{As}\left\langle\begin{array}{l}CH_3\\CH_3\\Cl\end{array}\right. + BaS = BaCl_2 + S\left\langle\begin{array}{l}As(CH_3)_2\\As(CH_3)_2\end{array}\right.$$

as a colourless, heavy, oily liquid, which mixes with alcohol and ether. Its odour is penetrating and resembles both alkarsin and mercaptan. The boiling point is above 100°. With hydrochloric acid it gives cacodylic chloride and hydric sulphide.

Cacodylic persulphide, cacodylic sulpho-cacodylate:



$$[As(CH_3)_2]_2S_2 = \mathrm{As}\left\langle\begin{array}{l}CH_3\\CH_3\\=S\\S\text{——}\mathrm{As}\left\langle\begin{array}{l}CH_3\\CH_3\end{array}\right.\end{array}\right.$$

corresponding to cacodylic cacodylate, is formed from the preceding by direct addition of sulphur, as also from cacodyl. It crystallises in colourless rhombic tables, which are readily soluble in alcohol, difficultly in water, and insoluble in ether, and which melt at 50°. If an alcoholic solution be mixed with alcoholic plumbic acetate, insoluble plumbic sulpho-cacodylate separates in colourless nacreous scales, whilst the solution contains cacodylic acetate:

$$2[As(CH_3)_2S.S.As(CH_3)_2] + Pb(O.C_2H_3O)_2$$
$$= \left.\begin{array}{l}As(CH_3)_2S.S\\As(CH_3)_2S.S\end{array}\right\rangle Pb + 2As(CH_3)_2.O.C_2H_3O.$$

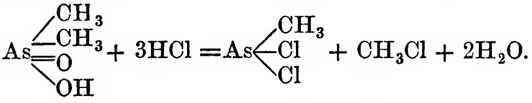
Other salts of sulpho-cacodylic acid have also been prepared, but all attempts to separate the free acid, $As(CH_3)_2S.SH$, have so far been unsuccessful.

326. Several of the *diethyl-arsen compounds* or *ethyl-cacodyl derivatives* have been prepared. They correspond in method of preparation and properties to the methyl bodies. The starting point is *diarsen-tetrethyl,* $As_2(C_2H_5)_4$, or *ethyl cacodyl,* which results, together with triethyl arsine, from the action of ethylic iodide upon sodic arsenide, and on fractional distillation of the product passes over last. It is a yellowish, heavy liquid, boiling between 185° and 195°, of garlic odour, and is spontaneously inflammable in air. It unites directly with oxygen, sulphur, and the halogens. By addition of iodine, e.g. *diethyl-arsen iodide*, $As(C_2H_5)_2I$, is obtained as a yellowish oil insoluble in water.

On allowing a dilute alcoholic solution of ethyl cacodyl to remain for a long time exposed to the air, it is slowly converted into *diethyl arsonic acid*, $As(C_2H_5)_2O.OH$. On evaporation it is obtained in strongly acid crystals, which deliquesce in moist air.

Arsen-monomethyl Compounds.

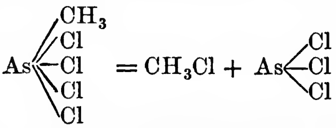
327. Of the monalkyl-arsen derivatives only those of methyl have been obtained in a state of purity and investigated. If cacodylic trichloride be submitted to distillation (§ 322) it evolves methylic chloride gas; and arsen-methyl dichloride, $As(CH_3)Cl_2$, condenses in the receiver as a heavy, colourless, strongly refractive liquid, which boils at 133° and is pretty soluble in water. Its vapour attacks the mucous membrane violently. It is also formed by the distillation of cacodylic acid in an atmosphere of hydrochloric acid :



$$As\left\langle\begin{array}{l}CH_3\\CH_3\\=O\\OH\end{array}\right. + 3HCl = As\left\langle\begin{array}{l}CH_3\\Cl\\Cl\end{array}\right. + CH_3Cl + 2H_2O.$$

On passing chlorine into arsen-methyl dichloride, mixed with carbonic disulphide and cooled to −10°, there separates

Arsen-methyl tetrachloride, $As(CH_3)Cl_4$, in large crystals, which decompose at 0° into arsenious trichloride and methylic chloride :



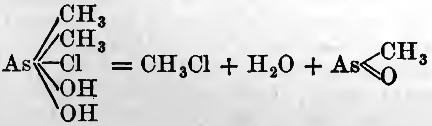
$$As\left\langle\begin{array}{l}CH_3\\Cl\\Cl\\Cl\\Cl\end{array}\right. = CH_3Cl + As\left\langle\begin{array}{l}Cl\\Cl\\Cl\end{array}\right.$$

328. If arsen-methyl dichloride be mixed with water and sodic carbonate, there is formed

Arsen-methyl oxide, $As\left\langle\begin{array}{l}CH_3\\O\end{array}\right.$, according to the equation :

$$As(CH_3)Cl_2 + Na_2CO_3 = 2NaCl + CO_2 + As(CH_3)O.$$

After evaporation of the water it is extracted from the residue by absolute alcohol, and is obtained by evaporation of the filtered liquid in short prisms, of indifferent reaction, little soluble in cold water and of 95° melting point. It is also formed on distilling arsen-dimethyl chloro-dihydrate, or cacodylic acid hydrochloride :



$$As\left\langle\begin{array}{l}CH_3\\CH_3\\Cl\\OH\\OH\end{array}\right. = CH_3Cl + H_2O + As\left\langle\begin{array}{l}CH_3\\O\end{array}\right.$$

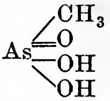
In the presence of aqueous vapour it volatilises. By the haloid acids and by sulphuretted hydrogen it is converted respectively into the haloid compounds and the sulphides.

Arsen-methyl diiodide, $As(CH_3)I_2$, crystallises in long brilliant yellow needles, which melt at 20° and distil unaltered at above 200°.

Arsen-methyl sulphide, $As(CH_3)S$, forms brilliant leaves or prisms, which melt at 110°.

329. On treating a mixture of arsen-methyl oxide and water with mercuric oxide, mercury separates, and the solution contains the mercuric salt of

Methyl arsinic acid,



$$\mathrm{As}\begin{cases}CH_3\\ =O\\ OH\\ OH\end{cases}$$

. This dibasic acid, corresponding to methyl phosphinic acid (§ 304), is usually obtained in the free state by addition of the requisite quantity of sulphuric acid to the baric salt. By evaporation of its aqueous solution it is obtained in large spear-shaped laminæ, composed of small dendritic needles of agreeable acid taste. *Baric methyl arsinate*, $As(CH_3)O{<}^{O}_{O}{>}Ba$, is obtained from the mercuric salt by addition of baric hydrate until all mercuric oxide is precipitated and evaporation of the filtrate. From its dilute aqueous solution alcohol precipitates the same salt with five molecules of water of crystallisation in colourless needles. The silver salt, $As(CH_3)O.(OAg)_2$, is precipitated from solutions of the baric salt in nacreous crystals, which detonate at 100°.

ANTIMONY COMPOUNDS OF THE ALCOHOL RADICALS.

330. Only those antimony compounds corresponding to the tertiary arsines and quaternary arsonium compounds are known. They are in nearly all respects analogous to these bodies.

They are prepared by action of alkylic iodides upon potassic antimonide. This alloy is best prepared by carbonising tartar emetic (potassic antimonylic tartrate) and strongly heating the product in covered vessels.

The reaction between the finely powdered alloy and the alkylic iodide is accompanied with great evolution of heat. The resulting tertiary stibine is then—if its boiling point be not too high—distilled off in vessels filled with carbonic anhydride, whilst potassic iodide and excess of antimony remain behind:

$$SbK_3 + 3C_nH_{2n+1}I = Sb(C_nH_{2n+1})_3 + 3KI.$$

The tertiary stibines oxidise rapidly—often spontaneously inflaming—on exposure to air, forming the oxides $Sb(C_nH_{2n+1})_3O$, which have the properties of a diacid basic anhydride, and yield hydric and normal salts with acids.

Similarly to their behaviour with oxygen, the tertiary stibines unite directly with one atom of sulphur or two atoms of halogen, and further unite with the elements of a molecule of an alkylic iodide to quaternary stibonium iodides, $Sb(C_nH_{2n+1})_4I$, from which, by action of argentic oxide, the caustic, alkaline monacid bases, $Sb(C_nH_{2n+1})_4.OH$, can be prepared.

Antimon-methyl Compounds.

331. *Trimethyl stibine*, or *antimon-trimethyl*, $Sb(CH_3)_3$, is obtained, by heating methylic iodide with potassic stibide, as a heavy, colourless liquid, insoluble in water, little soluble in alcohol, but readily in ether. Exposed to air, it fumes and soon inflames spontaneously. Its oxide, sulphide, and halogen compounds have been prepared, but not thoroughly investigated; they completely resemble those of trimethyl stibine. *Trimethyl-stibine diiodide*, $Sb(CH_3)_3I_2$, can be also prepared in beautiful crystals by direct heating of powdered antimony with methylic iodide at 140°:

$$Sb_4 + 9CH_3I = 3Sb(CH_3)_3I_2 + SbI_3.$$

By bringing together trimethyl-stibine iodide and zinc methyl, and subsequent distillation, an oily liquid passes over between 96° and 100°, not spontaneously inflammable—*antimon-pentamethyl*—and is formed according to the equation:

$$Sb(CH_3)_3I_2 + Zn(CH_3)_2 = ZnI_2 + Sb(CH_3)_5.$$

332. If trimethyl stibine be mixed with methylic iodide, combination occurs without the aid of extraneous heat. A white hard mass of *tetramethyl stibonic iodide*, $Sb(CH_3)_4I$, is obtained, which dissolves in hot water, and on cooling separates in beautiful hexagonal tables. This compound is readily soluble in alcohol, difficultly in ether. On boiling the aqueous solution with argentic oxide, argentic iodide separates, and the filtered liquid yields on evaporation in vacuo a white crystalline deliquescent mass of *tetramethyl stibonic hydrate*, $Sb(CH_3)_4.OH$; this is a strong base, has a caustic action like that of potassic hydrate, and is readily soluble in alcohol. On slow heating it can be partially volatilised without decomposition. Its salts are obtained directly by neutralisation with acids, or by decomposition of the iodide with silver salts.

Tetramethyl stibonic chloride, $Sb(CH_3)_4Cl$, and the *bromide*, $Sb(CH_3)_4Br$, crystallise like the iodide in hexagonal tables; the first gives with platinic chloride an orange yellow crystalline precipitate of the formula $[Sb(CH_3)_4Cl]_2,PtCl_4$.

The *nitrate*, $Sb(CH_3)_4O.NO_2$, prepared by double decomposition of the iodide with argentic nitrate, crystallises in readily soluble prisms, like those of potassic nitrate.

The sulphates are prepared from the hydrate and sulphuric acid. The *normal sulphate*, $[Sb(CH_3)_4]_2SO_4,5H_2O$, forms rhombic efflorescent crystals, of neutral reaction; the *hydric sulphate*, $Sb(CH_3)_4.HSO_4$, transparent hard tables of strongly acid reaction.

Both carbonates are known and are prepared like those of the alkali metals. The *normal carbonate*, $[Sb(CH_3)_4]_2CO_3$, is an indistinctly crystalline mass of alkaline reaction; the *acid salt*, $[Sb(CH_3)_4]HCO_3$, crystallises in star-like groups of needles, which are deliquescent and of alkaline reaction.

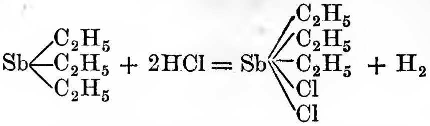
Antimon-ethyl Compounds.

333. *Triethyl stibine*, or *antimon-triethyl*, $Sb(C_2H_5)_3$, is obtained by the above-given method as a colourless liquid of sp. gr. 1·324 and 158° boiling point; it fumes in air and easily inflames spontaneously.

It is insoluble in water, miscible in every proportion with alcohol and ether.

With the halogens triethyl stibine combines with great evolution of heat, so that the ingredients can only be brought together in strongly diluted alcoholic or ethereal solutions.

Triethyl-stibine dichloride, $Sb(C_2H_5)_3Cl_2$, is obtained by heating triethyl stibine with concentrated hydrochloric acid, hydrogen being evolved. *Triethyl stibine therefore behaves like a strongly positive divalent metal:*



$$\mathrm{Sb}\left\langle\begin{matrix}C_2H_5\\C_2H_5\\C_2H_5\end{matrix}\right. + 2HCl = \mathrm{Sb}\left\langle\begin{matrix}C_2H_5\\C_2H_5\\C_2H_5\\Cl\\Cl\end{matrix}\right. + H_2$$

This dichloride is a colourless, strongly refractive liquid of sp. gr. 1·54. It smells like turpentine, tastes bitter, is insoluble in water, but soluble in alcohol and ether.

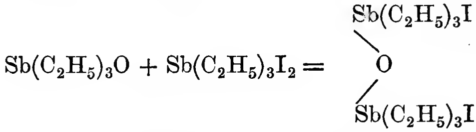
The *dibromide*, $Sb(C_2H_5)_3Br_2$, resembles the chloride, but solidifies at $-10°$ to a snow-white crystalline mass.

The *diiodide*, $Sb(C_2H_5)_3I_2$, forms colourless needles, melting at 70°.

If an ethereal solution of triethyl stibine be exposed to the air as long as oxygen is absorbed, there remains on evaporation of the solution

334. *Triethyl-stibine oxide*, or *antimon-triethyl oxide*, $Sb(C_2H_5)_3O$, as a viscous, colourless, amorphous mass, easily soluble in water and alcohol, less readily in ether.

On bringing together the oxide and diiodide of triethyl stibine in alcoholic solution, there crystallises on evaporation *triethyl-stibine oxyiodide* in vitreous octahedra and tetrahedra, soluble in water:

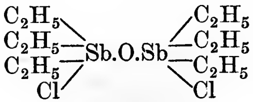


$$Sb(C_2H_5)_3O + Sb(C_2H_5)_3I_2 = \begin{matrix}Sb(C_2H_5)_3I\\ \diagdown\\ O\\ \diagup\\ Sb(C_2H_5)_3I\end{matrix}$$

The same compound is also obtained by evaporation of an alcoholic solution of the diiodide with ammonia:

$$2Sb(C_2H_5)_3I_2 + 2NH_3 + OH_2 = 2NH_4I + [Sb(C_2H_5)_3I]_2O.$$

By decomposition of the oxyiodide with mercuric chloride, mercuric iodide separates, and the analogous *triethyl-stibine oxychloride:*

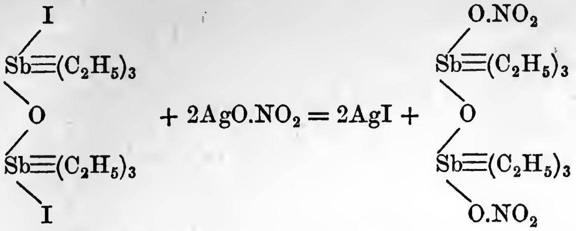


$$\left.\begin{matrix}C_2H_5\\C_2H_5\\C_2H_5\\Cl\end{matrix}\right\rangle Sb.O.Sb\left\langle\begin{matrix}C_2H_5\\C_2H_5\\C_2H_5\\Cl\end{matrix}\right.$$

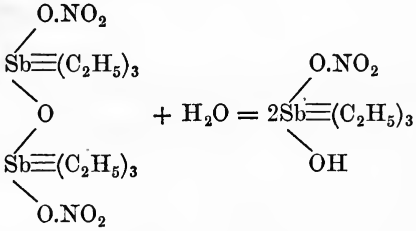
is formed, and remains on evaporation as a very deliquescent white fibro-crystalline mass. An *oxybromide* of like composition is also known.

335. *Triethyl-stibine Salts.*—With acids triethyl-stibine oxide yields basic and normal salts.

The *basic triethyl-stibine* salts are generally prepared by double decomposition of the oxyiodide with silver salts, and after filtration from the argentic iodide are obtained in the crystalline form by evaporation in vacuo:



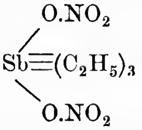
But water appears to be taken up at the same time, so that hydrated basic salts result:



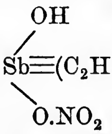
The normal salts are obtained from the basic, or from triethyl-stibine oxide, by addition of acids.

Sulphates.—The *normal sulphate*, $[Sb(C_2H_5)_3]SO_4$, crystallises from the syrupy solution in small white crystals, which melt at 100°; the *basic salt*, $[Sb(C_2H_5)_3OH]_2SO_4$, is a deliquescent gum-like mass.

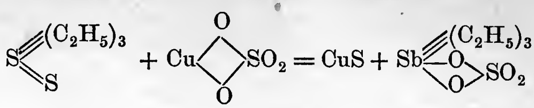
Nitrates.—The *normal nitrate*, $[Sb(C_2H_5)_3].(ONO_2)_2$, or



crystallises in large rhombic prisms, which melt at 62·5°. It dissolves readily in water, difficultly in alcohol, and explodes on heating. Its solution reddens blue litmus paper.

Basic triethyl-stibine nitrate, , is obtained in the form of a radiating crystalline mass, which is not deliquescent, but is readily soluble.

336. *Triethyl-stibine sulphide*, $Sb(C_2H_5)_3S$, is readily obtained by boiling an ethereal solution of triethyl stibine with sulphur, and separates on cooling in voluminous silvery crystals, which have a disagreeable odour and melt above 100°. Dilute acids decompose it into triethyl-stibine salts, with evolution of sulphuretted hydrogen. The aqueous solution gives with the salts of the heavy metals precipitates of metallic sulphides, whilst triethyl-stibine salts remain in solution :



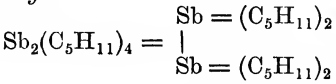
337. *Antimon-tetrethyl or Tetrethyl Stibonic Compounds.*—A mixture of equal molecules of triethyl stibine and ethylic iodide, when covered with water, slowly solidifies to tetrethyl stibonic iodide, $Sb(C_2H_5)_4I$, which by recrystallisation from hot water is obtained in large prisms or needles. By means of argentic oxide it is converted into *tetrethyl stibonic hydrate*, $Sb(C_2H_5)_4.OH$, a strongly alkaline syrupy liquid, which, with acids, yields neutral, readily soluble salts, which are mostly crystallisable. As they resemble those of tetramethyl stibonium in all respects, they may be passed over.

Methyl-triethyl stibonic iodide, $Sb(C_2H_5)_3(CH_3)I$, is obtained by direct combination of triethyl stibine with methylic iodide.

Amyl Compounds.

338. By action of isoamylic iodide upon potassic stibide *triisoamyl stibine* is formed, which cannot be separated by distillation, but must be extracted from the product by ether; on evaporation of the filtered solution it is obtained as a transparent yellowish liquid of sp. gr. 1·133. It fumes strongly in the air, but does not inflame spontaneously. With two atoms of halogen it yields compounds which are insoluble in water.

On endeavouring to distil this body a liquid passes over which on heating to 80° evolves an antimonial inflammable gas, and leaves *diantimon-tetrisoamyl :*



$$Sb_2(C_5H_{11})_4 = \begin{array}{l} Sb = (C_5H_{11})_2 \\ | \\ Sb = (C_5H_{11})_2 \end{array}$$

as a liquid not fuming in the air, but which slowly oxidises. It corresponds to the cacodyls in the arsenic compounds.

BISMUTH COMPOUNDS OF THE ALCOHOL RADICALS.

339. The only bismuth compounds yet prepared are the very unstable ethyl derivatives. By bringing together potassic bismuthide (prepared by strong heating of a mixture of twenty parts of bismuth with sixteen parts of powdered acid potassic tartrate in a Hessian crucible) with ethylic iodide, a rather violent reaction occurs. The cooled mixed product :

$$BiK_3 + 3C_2H_5I = 3KI + Bi(C_2H_5)_3,$$

after soaking with water, is shaken with ether. The latter removes

Bismuth triethyl, or *triethyl bismuthine*, $Bi(C_2H_5)_3$, which, after mixing with water and distilling off the ether, remains under the water as a yellowish mobile liquid of sp. gr. 1·82. Its smell is extremely disagreeable ; it fumes in the air and inflames spontaneously. Even below 100° it commences to decompose with evolution of gas and separation of metallic bismuth; at 150° it explodes violently.

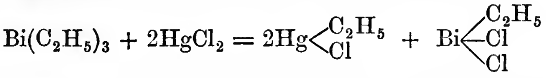
By slow oxidation, by long exposure of its alcoholic solution to air, bismuth triethyl is converted into bismuthous hydrate; by boiling with sulphur bismuth sulphide separates, whilst diethylic sulphide is evolved:

$$2Bi(C_2H_5)_3 + 6S = Bi_2S_3 + 3(C_2H_5)_2S.$$

A dilute alcoholic solution of bismuth triethyl to which iodine is slowly added yields, by combination with the latter, not pure bismuth triethyl-diiodide, but a compound of the latter with bismuthous iodide, $Bi(C_2H_5)_3I_2,BiI_3 = Bi_2(C_2H_5)_3I_5$. It is still more readily decomposed by chlorine and bromine.

340. On mixing an alcoholic solution of bismuth triethyl, slightly acidified with hydrochloric acid, with mercuric chloride, mercuric ethyl-chloride separates, whilst

Bismuth ethyl-dichloride, $Bi(C_2H_5)Cl_2$, remains in solution, and is obtained by evaporation of the filtered liquid in small colourless crystals. Its formation is represented by the equation:



$$Bi(C_2H_5)_3 + 2HgCl_2 = 2Hg\begin{cases}C_2H_5\\Cl\end{cases} + Bi\begin{cases}C_2H_5\\Cl\\Cl\end{cases}$$

The alcoholic solution of this compound gives, on heating with potassic iodide, potassic chloride and

Bismuth ethyl-diiodide, $Bi(C_2H_5)I_2$. If the liquid be mixed with water until strongly clouded, and then heated until again clear, bismuth ethyl-diiodide crystallises in golden yellow hexagonal plates. From its alcoholic solution potassic hydrate precipitates

Bismuth ethyl-oxide, $Bi(C_2H_5)O$, as an amorphous yellow powder, which in the dry state inflames when exposed to air. Argentic nitrate gives with bismuth ethyl-diiodide together with argentic iodide

Bismuth ethyl-dinitrate, $Bi(C_2H_5)(O.NO_2)_2$, which is obtained by evaporation in vacuo as a radiated crystalline mass, explodes at 40° and is slowly converted by water into basic bismuthous nitrate.

BORON COMPOUNDS OF THE ALCOHOL RADICALS.

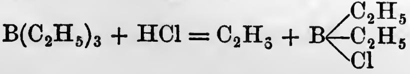
341. By mixing ethylic orthoborate (§ 224) with organo-zinc compounds in an atmosphere of carbonic anhydride, zinc ethylate separates, whilst an organo-boron compound is formed, which is obtained pure by distillation:

$$2B(OC_2H_5)_3 + 3Zn(C_nH_{2n+1})_2 = 3Zn(OC_2H_5)_2 + 2B(C_nH_{2n+1})_3.$$

Boron trimethyl, $B(CH_3)_3$, is a colourless gas of 1·93 density, and can be liquefied by pressure and cold.

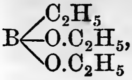
Boron triethyl, $B(C_2H_5)_3$, is a colourless, mobile liquid of very pungent irritant odour. Its sp. gr. is ·696 at 23°. It boils at 95° and has a vapour density 3·4. It inflames spontaneously in air and burns with a green flame. It is only slowly altered by water; by hydrochloric acid on heating it is converted into ethane and

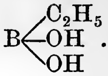
Boron diethyl-chloride, $B(C_2H_5)_2Cl$:



$$B(C_2H_5)_3 + HCl = C_2H_6 + B\begin{cases}C_2H_5\\C_2H_5\\Cl\end{cases}$$

If air be allowed to slowly gain access to boron triethyl it absorbs one molecule of oxygen and is converted into

Boron ethyl-diethylate,  $B\begin{cases}C_2H_5\\O.C_2H_5\\O.C_2H_5\end{cases}$, a liquid boiling at 125°, and which is at once converted by water into

Ethyl boric acid, or *boron ethyl-dihydrate*,  $B\begin{cases}C_2H_5\\OH\\OH\end{cases}$. This latter compound is removed from the aqueous solution by shaking with ether. By evaporation of the ether in a stream of carbonic anhydride the ethyl boric acid remains in the form of colourless leaves of an agreeable ethereal odour, sweet taste, acid reaction, and which begin to sublime at 40°.

SILICON COMPOUNDS OF THE ALCOHOL RADICALS.

342. The tetravalent element silicon combines with the alcohol radicals in four different proportions. Of the respective compounds only one series, $Si(C_nH_{2n+1})_4$, occur as free molecules, in all the other compounds poorer in alcohol radicals the silicon being further united to tetrad saturation with negative elements (oxygen or halogen).

The respective compounds show, in accordance with the similarity between carbon and silicon, certain analogies with such organic bodies as contain a carbon atom instead of the silicon atom, but are otherwise of like composition.

Silicon tri-, di-, and monalcohol radical compounds are obtained by heating ethylic orthosilicate (§ 225) with organo-zinc compounds and sodium. The latter cannot be dispensed with, as the zinc compounds of the alcohol radicals are without action on the orthosilicates. During the reaction metallic zinc separates, and therefore it is not organo-zinc but organo-sodium compounds which effect the substitution of the $O.C_2H_5$ group by alcohol radicals. The first reaction is probably:

$$2Si(OC_2H_5)_4 + Zn(C_2H_5)_2 + Na_2 = Zn + 2NaOC_2H_5 \\ + 2Si(C_2H_5)(C_2H_5O)_3.$$

By employment of larger quantities of zinc ethyl and sodium and a longer continuance of the action, the substitution is greater:

$$Si(OC_2H_5)_4 + Zn(C_2H_5)_2 + Na_2 = Zn + 2NaOC_2H_5 \\ + Si(C_2H_5)_2(C_2H_5O)_2$$

$$2Si(OC_2H_5)_4 + 3Zn(C_2H_5)_2 + 3Na_2 = 3Zn + 6NaOC_2H_5 \\ + 2Si(C_2H_5)_3(C_2H_5O).$$

A single one of the respective products is, however, never obtained, but invariably a mixture, from which the pure compounds must be separated by fractional distillation.

Silicon Tetralkyls, $Si(C_nH_{2n+1})_4$.

343. These compounds, which correspond to paraffins containing a quaternary united carbon atom, $C(C_nH_{2n+1})_4$, are obtained by heating silicic chloride with the zinc compounds of the alcohol radicals in sealed tubes to 130°–200°:

$$SiCl_4 + 2Zn(C_nH_{2n+1})_2 = 2ZnCl_2 + Si(C_nH_{2n+1})_4.$$

When the reaction is completed they are distilled from the zincic chloride, shaken with solution of potassic hydrate in order to destroy any organo-zinc compound or silicic chloride, and then dried by means of calcic chloride and rectified.

So far as known they are all liquids which are not affected by exposure to air.

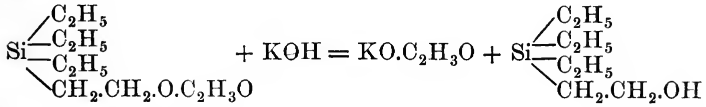
Silicon tetramethyl, $Si(CH_3)_4$, is a colourless, mobile liquid, which boils at 30°–31°, floats on water, and at higher temperatures burns with a clear flame and formation of white fumes consisting of silicic anhydride. Its vapour density is 3·058.

Silicon tetrethyl, $Si(C_2H_5)_4$, is also a liquid lighter than water, which boils at 153°. The vapour density is 5·13.

Its behaviour with chlorine is peculiar; this, on being passed into cooled silicon tetrethyl, does not split off ethyl groups, but replaces hydrogen; the first action is:

$$Si(C_2H_5)_4 + Cl_2 = HCl + Si(C_2H_5)_3(C_2H_4Cl).$$

This latter body is a liquid boiling at 185°. It corresponds to a nonylic chloride, $C_9H_{19}Cl = C(C_2H_5)_3.C_2H_4Cl$, and is therefore termed *siliconoylic chloride*. With potassic acetate it yields potassic chloride and *siliconoylic acetate*, $Si(C_2H_5)_3(C_2H_4.O.C_2H_3O)$, which boils at about 212°, and by heating with alcoholic potassic hydrate is saponified, giving *siliconoylic alcohol*, $Si(C_2H_5)_3(C_2H_4.OH)$:



$$Si\begin{cases}C_2H_5\\C_2H_5\\C_2H_5\\CH_2.CH_2.O.C_2H_3O\end{cases} + KOH = KO.C_2H_3O + Si\begin{cases}C_2H_5\\C_2H_5\\C_2H_5\\CH_2.CH_2.OH\end{cases}$$

Silicononylic alcohol is a liquid of camphor-like odour, insoluble in water, boiling at 190°. It corresponds to a nonylic alcohol:

$$C(C_2H_5)_3.CH_2.CH_2.OH,$$

which is still unknown.

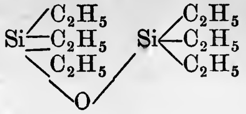
Silicon Triethyl or Triethyl-silicyl Compounds.

344. If tetrethylic silicate be heated for a long time with large quantities of zinc ethyl and sodium in sealed tubes to 200° there can be isolated, by repeated fractional distillation of the product,

Silicon triethyl-ethylate, $Si(C_2H_5)_3.O.C_2H_5$, as a colourless liquid boiling at 153°. The vapour density is 5·57, the sp. gr. ·8414 at 0°. On mixing with aqueous distilled hydriodic acid heat is evolved, and a rather violent reaction occurs, in which ethylic iodide, water, and silicon triethyl-oxide are formed:

$$2Si(C_2H_5)_3(OC_2H_5) + 2HI + 2C_2H_5I + H_2O + [Si(C_2H_5)_3]_2O.$$

Silicon triethyl-oxide, silico-heptyl oxide, or *triethyl-silicyl ether:*



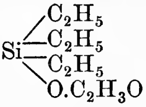
is a colourless liquid, which boils between 224° and 229°, and has at 0° sp. gr. ·8831.

If silicon triethyl-ethylate be heated for a long time at 280° with acetic anhydride, there results, according to the equation:

$$Si(C_2H_5)_3(OC_2H_5) + (C_2H_3O)_2O = C_2H_5.O.C_2H_3O + Si(C_2H_5)_3O.C_2H_3O,$$

ethylic acetate, together with

Silicon triethyl-acetate, triethyl-silicol acetate:

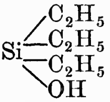


as an agreeable-smelling liquid of sp. gr. ·9039 at 0°, which boils at 168°. By boiling with concentrated sodic hydrate this body is decomposed according to the equation:

$$2Si(C_2H_5)_3.O.C_2H_3O + Na_2CO_3 + H_2O = 2NaO.C_2H_3O + CO_2 + 2Si(C_2H_5)_3OH.$$

The body so obtained,

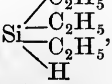
Triethyl silicol, silicon triethyl-hydrate, or *triethyl silicic hydrate:*



is an oil having the properties of a tertiary alcohol, and which is of analogous composition to the tertiary heptyl alcohol, triethyl carbinol, $C(C_2H_5)_3OH$. If its ethereal solution be treated with sodium, the latter dissolves with evolution of hydrogen and formation of sodic triethyl silicolate, $Si(C_2H_5)_3.O.Na$.

On endeavouring, by renewed action of zinc ethyl and sodium on silicon triethyl-ethylate, to replace the last ethoxyl group by ethyl, ethylene is evolved, and there is formed, according to the equation:

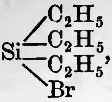
$$2Si(C_2H_5)_3.O.C_2H_5 + Zn(C_2H_5)_2 + Na_2 = Zn + 2Na(OC_2H_5) + 2C_2H_4 + 2Si(C_2H_5)_3H,$$

Silicon triethyl-hydride, , or silico-heptane, an analogue of the heptane triethyl methane. It is a colourless liquid, insoluble in water, of petroleum-like odour, boils at 107°, and at 0° has sp. gr. ·751.

Bromine reacts very violently upon silico-heptane, and forms, according to the equation :

$$Si(C_2H_5)_3H + Br_2 = 2HBr + Si(C_2H_5)_3Br,$$

Triethyl silicic bromide,



$$\mathrm{Si}\begin{cases}C_2H_5\\C_2H_5\\C_2H_5\\Br\end{cases}$$

a liquid boiling at 163°, which fumes in the air and is slowly decomposed by water into triethyl silicol :

$$Si(C_2H_5)_3Br + H_2O = HBr + Si(C_2H_5)_3.OH,$$

and triethyl silicic ether :

$$2Si(C_2H_5)_3Br + H_2O = 2HBr + [Si(C_2H_5)_3]_2O.$$

Triethyl silicol, with its derivatives, is of great theoretical interest as the first complete example of a true silicon alcohol.

Silicon Diethyl Compounds.

345. By heating one molecule of tetrethylic silicate with one molecule of zinc ethyl, and sodium, in sealed glass tubes, the chief product formed is

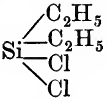
Silicon diethyl-diethylate, or the so-called *silicon diethyl-ketone ether*, $Si(C_2H_5)_2(OC_2H_5)_2$, a liquid insoluble in water, but soluble in alcohol and ether, whose boiling point is 155·5°. Its sp. gr. at 0° = ·8752, its vapour density 6·19. By heating with acetyl chloride in sealed tubes to 200° it is converted, according to the equation :

$$Si(C_2H_5)_2(OC_2H_5)_2 + C_2H_3O.Cl = C_2H_5.O.C_2H_3O + Si(C_2H_5)_2(O.C_2H_5)Cl,$$

into *silicon diethyl-ethylate chloride*, and further :

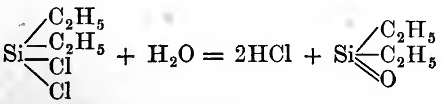
$$Si(C_2H_5)_2(O.C_2H_5)Cl + C_2H_3OCl = C_2H_5.O.C_2H_3O + Si(C_2H_5)_2Cl_2,$$

into *silicon diethyl-dichloride :*



$$\mathrm{Si}\begin{cases}C_2H_5\\C_2H_5\\Cl\\Cl\end{cases}$$

Both compounds are liquids which fume in the air; the first boils at 148°, the latter at 129°. This body, by treatment with water, is converted into :



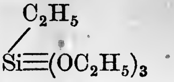
$$\mathrm{Si}\begin{cases}C_2H_5\\C_2H_5\\Cl\\Cl\end{cases} + H_2O = 2HCl + \mathrm{Si}\begin{cases}C_2H_5\\C_2H_5\\O\end{cases}$$

Silicon diethyl-oxide, or *diethyl silicon ketone*, $Si(C_2H_5)_2O$, a viscous liquid boiling above 360°.

Silicon Monethyl Compounds.

346. The first product of the simultaneous decomposition of ethylic orthosilicate and zinc ethyl by sodium (which takes place even in open vessels) is

Silicon ethyl-triethylate, or *ethylic orthosilico-propionate:*



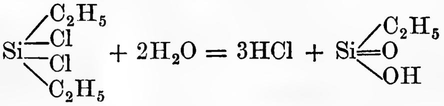
When purified by fractional distillation the compound is obtained as an ethereal liquid of agreeable odour, boiling at 159°, insoluble in water, though slowly altered by it. By heating with three molecules of acetic chloride to 180° it forms

Silicon ethyl-trichloride, $Si(C_2H_5)Cl_3$, a liquid boiling between 90° and 110°:

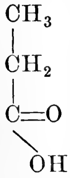
$$Si(C_2H_5)(O.C_2H_5)_3 + 3C_2H_3O.Cl = 3C_2H_5.O.C_2H_3O + Si(C_2H_5)Cl_3,$$

which is slowly converted by water into

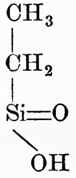
Silicon ethyl-oxyhydrate, $Si(C_2H_5)O.OH$:



This latter compound forms an insoluble white powder; on heating in air it smoulders, leaving carbonaceous silicic anhydride. It is dissolved by potassic hydrate, probably forming the salt $Si(C_2H_5)O.OK$. In its constitution this weak acid corresponds to propionic acid, and is therefore designated *silico-propionic acid:*



Propionic acid.



Silico-propionic acid.

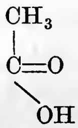
347. Zinc methyl and sodium act only with great difficulty on ethylic orthosilicate. The mixture must be heated for a long time, finally to 300°, when, according to the equation:

$$2Si(OC_2H_5)_4 + Zn(CH_3)_2 + Na_2 = 2NaO.C_2H_5 + Zn + 2Si(CH_3)(C_2H_5O)_3,$$

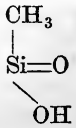
silicon methyl-triethylate is formed. This boils at 145°–151°, and on treatment with hydriodic acid is converted into *silicon methyl-oxyhydrate:*

$$Si(CH_3)(C_2H_5O)_3 + 3HI = 3C_2H_5I + H_2O + Si(CH_3)O.OH.$$

This latter compound is insoluble in water, smoulders on heating in air, has the properties of a weak acid, and, on account of the analogy of its constitution to that of acetic acid, is termed *silico-acetic acid.*



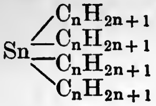
Acetic acid.



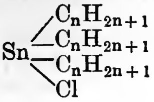
Silico-acetic acid.

TIN COMPOUNDS OF THE ALCOHOL RADICALS.

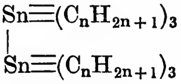
348. Tin unites with two, three, or four alcohol radicals, but only the bodies of the last group :



occur as simple molecules, whilst the tri and di derivatives occur as radicals in combination with other elements, or united with a further quantity of themselves, forming complex molecules :

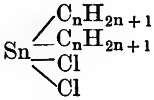


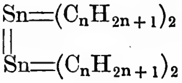
Chloride.



$$\begin{array}{l} Sn\equiv(C_nH_{2n+1})_3 \\ | \\ Sn\equiv(C_nH_{2n+1})_3 \end{array}$$

Free molecule.





$$\begin{array}{l} Sn=(C_nH_{2n+1})_2 \\ \| \\ Sn=(C_nH_{2n+1})_2 \end{array}$$

so that the tin in all these compounds behaves as a tetrad.

The ethyl compounds have been most investigated.

349. The tin ethyl compounds can be conveniently prepared by action of ethylic iodide upon the alloy prepared by fusing together sodium and tin. This latter is powdered and placed in a flask provided with an inverted condenser, covered with the iodide, and the reaction started by application of a gentle heat. Once commenced, it proceeds with such energy that the flask must be cooled by immersion in water. When the temperature falls the reaction is completed by heating.

Different compounds are obtained according to the amount of sodium in the alloy and to the proportion of the different ingredients present.

By employment of an alloy very poor in sodium, and an excess of ethylic iodide, *stan-diethyl diiodide*, $Sn(C_2H_5)_2I_2$, and *stan-triethyl iodide*, $Sn(C_2H_5)_3I$, are mainly formed, the latter being formed in larger quantity the larger the amount of sodium in the alloy. If the amount of sodium reaches 20 % there are obtained only the free radicals *distan-tetrethyl*, $Sn_2(C_2H_5)_4$, and *distan-hexethyl*, $Sn_2(C_2H_5)_6$. These latter are extracted from the mixed products, which contain sodic iodide and excess of zinc, by means of ether, and are obtained mixed together on evaporation of the filtered solution in an atmosphere of carbonic anhydride. They can be separated by means of alcohol, in which distan-hexethyl is scarcely soluble, whilst distan-tetrethyl is readily dissolved.

On distilling the reaction-mass directly from the sand bath the distan-hexethyl passes over nearly unaltered, but distan-tetrethyl decomposes into tin and stan-tetrethyl, which volatilises. The two bodies in the distillate can be separated by fractional distillation.

Pure tin in the shape of tin filings only acts on ethylic iodide at high temperatures or in sunlight. Stan-diethyl diiodide is the main product:

$$Sn + 2C_2H_5I = Sn(C_2H_5)_2I_2.$$

Stan-tetrethyl is most conveniently prepared by careful mixing of two molecules of zinc ethyl with one molecule of stannic chloride and afterwards distilling:

$$SnCl_4 + 2Zn(C_2H_5)_2 = 2ZnCl_2 + Sn(C_2H_5)_4.$$

The halogen compounds of the radicals poorer in ethyl also yield stan-tetrethyl when treated with zinc ethyl:

$$Sn(C_2H_5)_2I_2 + Zn(C_2H_5)_2 = ZnI_2 + Sn(C_2H_5)_4.$$

350. The alcohol radicals united to tin can be easily replaced one after another by halogens. If, for instance, stan-tetrethyl be treated with a molecule of iodine, it yields ethylic iodide and stan-triethyl iodide:

$$Sn(C_2H_5)_4 + I_2 = C_2H_5I + Sn(C_2H_5)_3I.$$

This by more iodine is converted into stan-diethyl diiodide:

$$Sn(C_2H_5)_3I + I_2 = C_2H_5I + Sn(C_2H_5)_2I_2.$$

This latter on heating with iodine is converted into stannic iodide:

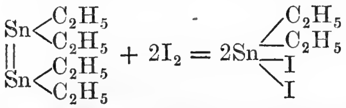
$$Sn(C_2H_5)_2I_2 + 2I_2 = 2C_2H_5I + SnI_4;$$

but so far attempts to prepare a stan-ethyl triiodide in this way have not met with success. Hydrochloric acid converts stan-tetrethyl into stan-ethyl chlorides and ethane:

$$Sn(C_2H_5)_4 + HCl = Sn(C_2H_5)_3Cl + C_2H_6$$
$$Sn(C_2H_5)_3Cl + HCl = Sn(C_2H_5)_2Cl_2 + C_2H_6.$$

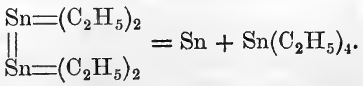
Stan-diethyl Compounds.

351. *Stan-diethyl*, or *distan-tetrethyl*, $Sn_2(C_2H_5)_4$. As mentioned above, distan-tetrethyl is separated from the distan-hexethyl formed at the same time by means of alcohol; from this solution it is precipitated by water as a colourless, thick, oily liquid of 1·558 sp. gr. From the air it absorbs oxygen, and similarly unites with the halogens to form stan-diethyl dihaloids; e.g.



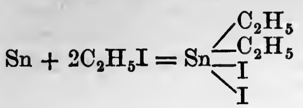
$$\begin{matrix} Sn{<}^{C_2H_5}_{C_2H_5} \\ \| \\ Sn{<}^{C_2H_5}_{C_2H_5} \end{matrix} + 2I_2 = 2Sn\begin{matrix} /C_2H_5 \\ \angle C_2H_5 \\ -I \\ \backslash I \end{matrix}$$

It is not volatile without decomposition; on heating it is converted, with separation of tin, into stan-tetrethyl, which distils over:



$$\begin{matrix} Sn{=}(C_2H_5)_2 \\ \| \\ Sn{=}(C_2H_5)_2 \end{matrix} = Sn + Sn(C_2H_5)_4.$$

The diiodide can be obtained directly by the action of ethylic iodide on poor sodium zinc alloy, as also from zinc filings and ethylic iodide on heating or exposure to the action of sunlight :



$$\mathrm{Sn} + 2\mathrm{C_2H_5I} = \mathrm{Sn}\begin{array}{l}\mathrm{C_2H_5}\\ \mathrm{C_2H_5}\\ \mathrm{I}\\ \mathrm{I}\end{array}$$

Stan-diethyl diiodide crystallises in colourless needles, melting at 44·5° and subliming on stronger heating. In water it is but little soluble, more readily in alcohol, readily in ether.

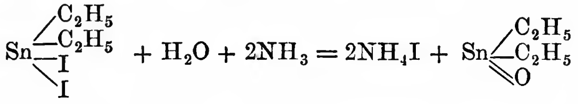
Stan-diethyl dichloride is best prepared by dissolving stan-diethyl oxide in hydrochloric acid and evaporation of the solution. It forms colourless needles, melting at 85°, boiling unaltered at 220°, and even sublimes on slightly heating. The vapour density is 8·553.

Both halogen compounds yield distan-tetrethyl when treated with zinc :

$$2\mathrm{Sn(C_2H_5)_2Cl_2} + 2\mathrm{Zn} = 2\mathrm{ZnCl_2} + \mathrm{Sn_2(C_2H_5)_4}.$$

In an aqueous solution of the dihaloids ammonia gives a precipitate of

Stan-diethyl oxide, $\mathrm{Sn(C_2H_5)_2O}$:

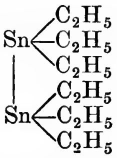


$$\mathrm{Sn}\begin{array}{l}\mathrm{C_2H_5}\\ \mathrm{C_2H_5}\\ \mathrm{I}\\ \mathrm{I}\end{array} + \mathrm{H_2O} + 2\mathrm{NH_3} = 2\mathrm{NH_4I} + \mathrm{Sn}\begin{array}{l}\mathrm{C_2H_5}\\ \mathrm{C_2H_5}\\ \mathrm{O}\end{array}$$

a white powder insoluble in water, alcohol, and ether, soluble in acids forming salts. The dinitrate, $\mathrm{Sn(C_2H_5)_2(O.NO_2)_2}$, crystallises in prisms; the sulphate, $\mathrm{Sn(C_2H_5)_2SO_4}$, in plates.

Stan-triethyl Compounds.

352. *Distan-hexethyl :*



$$\begin{array}{l}\mathrm{Sn}(\mathrm{C_2H_5})_3\\ |\\ \mathrm{Sn}(\mathrm{C_2H_5})_3\end{array}$$

is a thick liquid, insoluble in alcohol, but readily soluble in ether, boiling at 265°–270° with partial decomposition.

It can be obtained from stan-triethyl iodide by action of sodium :

$$2\mathrm{Sn(C_2H_5)_3I} + \mathrm{Na_2} = 2\mathrm{NaI} + \mathrm{Sn_2(C_2H_5)_6}.$$

Its sp. gr. at 0° = 1·4115, its vapour density = 14·70.

It is unaffected by the air. Its odour, like that of all stan-triethyl compounds, is peculiarly penetrating.

On passing chlorine into a solution of distan-hexethyl in chloroform, *stan-diethyl dichloride* is obtained, according to the equation :

$$\mathrm{Sn_2(C_2H_5)_6} + 3\mathrm{Cl_2} = 2\mathrm{Sn(C_2H_5)_2Cl_2} + 2\mathrm{C_2H_5Cl};$$

whilst iodine, when carefully added in the cold, gives stan-triethyl iodide :

$$\mathrm{Sn_2(C_2H_5)_6} + \mathrm{I_2} = 2\mathrm{Sn(C_2H_5)_3I}.$$

Stan-triethyl chloride, $Sn(C_2H_5)_3Cl$, is obtained most readily by action of hydrochloric acid on the oxide (compare § 350). It is an oily liquid, boiling at 209°, of sp. gr. 1·428, and solidifying in crystals at 0°. Its vapour acts violently on the mucous membrane.

Stan-triethyl iodide, $Sn(C_2H_5)_3I$, is prepared directly by aid of tin alloy poor in sodium, and is obtained in a state of purity by the fractional distillation of the product. It is a colourless oil of 1·85 sp. gr., boiling at 231°. It is miscible in all proportions with alcohol and ether.

If a solution of the halogen compound be decomposed by argentic oxide or potassic hydrate and distilled,

Stan-triethyl hydrate, $Sn(C_2H_5)_3.OH$, passes over along with the water vapour. It crystallises in brilliant colourless prisms, which melt at 43° and distil at 272°. It sublimes slowly at ordinary temperatures. It is only slightly dissolved by water, but readily by alcohol and ether. It reacts strongly alkaline, and absorbs carbonic anhydride from the air. If heated for a long time to near its boiling point it evolves water and leaves the anhydride

Stan-triethyl oxide, $[Sn(C_2H_5)_3]_2O$:

$$2Sn(C_2H_5)_3.OH = H_2O + [Sn(C_2H_5)_3].O.[Sn(C_2H_5)_3],$$

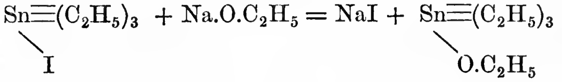
which by action of water again yields the hydrate.

The salts of stan-triethyl are mostly crystallisable, and can be prepared directly.

The *sulphate*, $[Sn(C_2H_5)_3]_2SO_4$, crystallises in brilliant colourless prisms, which are more soluble in cold than in boiling water. The *nitrate*, $Sn(C_2H_5)_3.O.NO_2$, is difficult to crystallise.

If stan-triethyl iodide be heated to 200° with dry sodic ethylate,

Stan-triethyl ethylate, $Sn(C_2H_5)_3(OC_2H_5)$, distils over as a colourless, unpleasant-smelling liquid, of 1·2634 sp. gr. at 0°, boiling at 190°–192°. It is formed according to the equation:



$$\underset{\diagdown\,I}{Sn{\equiv}(C_2H_5)_3} + Na.O.C_2H_5 = NaI + \underset{\diagdown\,O.C_2H_5}{Sn{\equiv}(C_2H_5)_3}$$

and decomposes with water to ethylic alcohol and stan-triethyl hydrate (§ 344).

353. *Stan-tetrethyl*, $Sn(C_2H_5)_4$. The method of preparation and most important reactions of this body have already been given. It is a colourless liquid of faint ethereal odour and somewhat metallic taste, boiling at 181°. Its sp. gr. is 1·187 at 13°, the vapour density 8·021.

354. Several of the methyl compounds of tin have been prepared; they resemble the corresponding ethyl compounds.

Stan-tetramethyl boils at 78°, has at 0° sp. gr. 1·3138 and a vapour density of 6·00. *Stan-trimethyl iodide*, $Sn(CH_3)_3I$, is liquid, smells like mustard oil, boils at 170°, and has sp. gr. 2·1432 at 0°. Treated with sodium it does not yield distan-hexmethyl, but is decomposed according to the equation

$$4Sn(CH_3)I + 2Na_2 = 4NaI + Sn + 3Sn(CH_3)_4.$$

Stan-trimethyl hydrate, $Sn(CH_3)_4.OH$, forms colourless prisms, very slightly soluble in water. It reacts strongly alkaline, and readily volatilises. Treated with acid it gives salts, and by long heating the anhydrous *oxide* $[Sn(CH_3)_3]_2O$.

Of the dimethyl compounds *distan-tetramethyl* has been prepared, but requires further investigation. *Stan-dimethyl diiodide*, $Sn(CH_3)_2I_2$, crystallises in prisms, melting at 22°, boiling at 228°, and pretty readily soluble in water. Ammonia precipitates from it amorphous *stan-dimethyl oxide*, insoluble in water, soluble in potassic hydrate, and yielding crystalline salts with the acids.

Compounds containing both ethyl and methyl are also known. Their formation is represented by the equations:

$$Sn(C_2H_5)_2Cl_2 + Zn(CH_3)_2 = ZnCl_2 + Sn(C_2H_5)_2(CH_3)_2$$

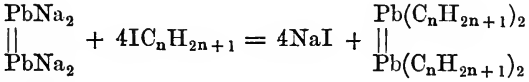
and $$2Sn(CH_3)_3Cl + Zn(C_2H_5)_2 = ZnCl_2 + 2Sn(CH_3)_3(C_2H_5).$$

355. Of normal propyl and isobutyl derivatives there have been prepared $Sn(C_3H_7)_3I$ as a liquid boiling at 269°–270°, and $Sn(C_4H_9)_3I$ as an oil boiling at 292°–296°. *Stan-triisobutyl hydrate* is solid, amorphous, volatile, and of strongly alkaline reaction.

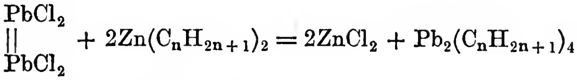
LEAD COMPOUNDS OF THE ALCOHOL RADICALS.

356. In most of its inorganic compounds lead acts as a diad element, but in its compounds with the alcohol radicals, as far as they are yet known, it behaves as a tetrad.

The compounds $Pb(C_nH_{2n+1})_4$ are prepared by action of alcoholic iodides upon an alloy of lead and sodium, or better by treatment of plumbic chloride with organo-zinc compounds, followed by distillation. Probably the diad compounds or the double molecule of the latter are first formed:

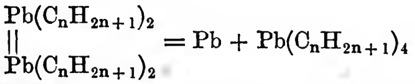


$$\begin{array}{l}PbNa_2\\ \|\\ PbNa_2\end{array} + 4IC_nH_{2n+1} = 4NaI + \begin{array}{l}Pb(C_nH_{2n+1})_2\\ \|\\ Pb(C_nH_{2n+1})_2\end{array}$$



$$\begin{array}{l}PbCl_2\\ \|\\ PbCl_2\end{array} + 2Zn(C_nH_{2n+1})_2 = 2ZnCl_2 + Pb_2(C_nH_{2n+1})_4$$

which yield lead and the tetrad compound at a far lower temperature than in the case of distan-tetrethyl:



$$\begin{array}{l}Pb(C_nH_{2n+1})_2\\ \|\\ Pb(C_nH_{2n+1})_2\end{array} = Pb + Pb(C_nH_{2n+1})_4$$

By halogens the latter are converted into alkylic haloids and monohaloid derivatives:

$$Pb(C_nH_{2n+1})_4 + I_2 = C_nH_{2n+1}I + Pb(C_nH_{2n+1})_3I\,;$$

by acids into paraffins and salts:

$$Pb(C_nH_{2n+1})_4 + HCl = C_nH_{2n+2} + Pb(C_nH_{2n+1})_3Cl$$

$$2Pb(C_nH_{2n+1})_4 + H_2SO_4 = 2C_nH_{2n+2} + [Pb(C_nH_{2n+1})_3]_2SO_4.$$

From these salts the strongly basic hydrates, $Pb(C_nH_{2n+1})_3OH$, can be obtained. Methyl, ethyl, and isoamyl compounds are known.

357. *Lead Methyl Compounds.*—On adding to perfectly dry plumbic chloride, contained in a distillation apparatus, filled with dried carbonic anhydride, a quantity of zinc methyl insufficient for complete decomposition, metallic lead separates, and on distillation *plumb-tetramethyl*, $Pb(CH_3)_4$, passes over as a colourless, mobile liquid, boiling at 110°. The sp. gr. is 2·034 at 0°, its found vapour density at 130° = 9·52 (theoretical 9·25). It is insoluble in pure water, but readily in alcohol and ether; it is not affected by atmospheric oxygen.

If plumbic tetramethyl be boiled for some time with hydrochloric acid there separates, on cooling, long silky needles of *plumb-trimethyl chloride*, $Pb(CH_3)_3Cl$, which can, when dry, be sublimed in a small glass tube.

By the decomposition of plumb-tetramethyl by careful addition of iodine, *plumb-trimethyl iodide*, $Pb(CH_3)_3I$, is obtained in colourless needles, little soluble in water, readily in boiling alcohol. If this be distilled with solid potassic hydrate, an oil smelling like mustard passes over, which solidifies to strongly alkaline prisms, probably of *plumb-trimethyl hydrate*, $Pb(CH_3)_3.OH$.

358. *Lead Ethyl Compounds.*—*Plumb-tetrethyl*, $Pb(C_2H_5)_4$, is usually prepared by decomposition of plumbic chloride with zinc ethyl, and distillation in vacuo of the liquid poured off the precipitated lead. It is a colourless liquid of 1·62 sp. gr., boiling with partial decomposition at above 200°. When heated in the air it burns with an orange-coloured, green-mantled flame. Boiled with hydrochloric acid, it gives *plumb-triethyl chloride*, $Pb(C_2H_5)_3Cl$, with evolution of ethane, and reacts with iodine to form the respective iodides:

$$Pb(C_2H_5)_4 + I_2 = Pb(C_2H_5)_3I + C_2H_5I.$$

Both haloid compounds crystallise in needles, are volatile, and smell like mustard oil. When distilled with solid potassic hydrate, *plumb-triethyl hydrate*, $Pb(C_2H_5)_3.OH$, passes over as an oily, strongly alkaline liquid, of powerful odour, which solidifies on cooling to a mass of interlaced needles. *Plumb-triethyl sulphate*, $[Pb(C_2H_5)_3]_2SO_4$, separates, on neutralisation of an aqueous solution of the hydrate with sulphuric acid, in difficultly soluble, hard, brilliant octahedra.

359. *Plumb-tetrisoamyl*, $Pb(C_5H_{11})_4$, is obtained, by action of isoamylic iodide upon lead-sodium alloy, extraction of the product with ether, and evaporation of the filtered solution, as a yellow oily liquid which cannot be distilled unaltered. *Plumbic triisoamyl iodide*, $Pb(C_5H_{11})_3I$, prepared from this, crystallises in colourless needles. The hydrate and chloride are also known.

Aluminium Compounds of the Alcohol Radicals.

360. On heating aluminium filings with ethylic iodide in sealed glass tubes to 130°–150°, there is obtained a thick liquid, spontaneously inflammable in air, and decomposed by water with explosive violence. This results from the direct union of the metals with the components of the ethylic iodide, and without doubt has the composition $Al_2(C_2H_5)_3I_3$. Pure aluminium ethyl cannot be obtained by distillation from this, the liquid distilling over invariably containing some iodine.

Organo-aluminium bodies can be obtained in a state of purity by digesting the corresponding mercury compounds with thin aluminium foil, this method serving especially for the preparation of the methyl and ethyl compounds. From the determinations of their vapour densities these bodies immediately above their boiling points must be expressed by the formula $Al_2(C_nH_{2n+1})_6$, being analogous to that of aluminic chloride; on increasing the temperature, however, the vapour density decreases and approaches to nearly half its former value, i.e. corresponds to the molecular formula $Al(C_nH_{2n+1})_3$. The organo-aluminium compounds fume in the air, readily inflame spontaneously, and then burn with evolution of thick fumes of alumina. Water decomposes them with explosive violence into paraffins and aluminic hydrate:

$$Al_2(C_nH_{2n+1})_6 + 6H_2O = Al_2(OH)_6 + 6C_nH_{2n+2}.$$

Aluminium methyl, $Al_2(CH_3)_6$ or $Al(CH_3)_3$, is obtained by digesting mercury dimethyl with aluminium foil and then distilling. It is liquid at ordinary temperatures, crystalline at 0°, and boils at 130°. Immediately above this temperature the vapour density is 4·35, at 160° only 3·9–4·1, and finally at 240° only 2·8. The theoretical density for $Al_2(CH_3)_6$ is 4·98; for $Al(CH_3)_3$, 2·49.

Aluminium ethyl, $Al_2(C_2H_5)_6$ or $Al(C_2H_5)_3$, obtained in similar manner to the methyl compound, is still liquid at −18° and boils at 194°. At 230° its vapour density is found to be 4·5. The vapour would therefore appear to be a mixture of a little $Al_2(C_2H_5)_6$ (theoretical density 7·88) with much $Al(CH_3)_3$ (theoretical density 3·94).

Mercury Compounds of the Alcohol Radicals.

361. Mercury forms saturated compounds with two alcohol radicals, $Hg(C_nH_{2n+1})_2$. They can be prepared by the action of organo-zinc compounds with mercuric chloride:

$$HgCl_2 + Zn(C_nH_{2n+1})_2 = ZnCl_2 + Hg(C_nH_{2n+1})_2;$$

and directly by the action of sodium amalgam, diluted with much mercury upon the alcoholic iodides, some ethylic acetate being generally also added:

$$HgNa_2 + 2IC_nH_{2n+1} = 2NaI + Hg(C_nH_{2n+1})_2.$$

By careful addition of halogens to these compounds one alcohol radical is removed and replaced by the halogen:

$$Hg(C_nH_{2n+1})_2 + I_2 = Hg(C_nH_{2n+1})I + C_nH_{2n+1}I;$$

but excess of halogen converts these into mercuric haloids:

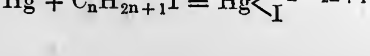
$$Hg(C_nH_{2n+1})I + I_2 = HgI_2 + C_nH_{2n+1}.I.$$

Halogen hydro-acids even in excess only cause the replacement of one alcohol radical:

$$Hg(C_nH_{2n+1})_2 + HCl = Hg(C_nH_{2n+1})Cl + C_nH_{2n+2}.$$

The oxy-acids act similarly and form corresponding salts.

The iodides can be prepared directly from the alcoholic iodides and mercury in presence of sunlight:

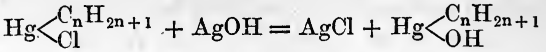


$$Hg + C_nH_{2n+1}I = Hg\begin{matrix} \diagup C_nH_{2n+1} \\ \diagdown I \end{matrix}$$

and can be converted into the diorgano-compound by heating with potassic cyanide :

$$2Hg(C_nH_{2n+1})I + 2KCN = 2KI + Hg + C_2N_2 + Hg(C_nH_{2n+1})_2.$$

If the haloid compounds be brought into contact with moist argentic oxide, the caustic basic hydrates are formed :



$$Hg{<}^{C_nH_{2n+1}}_{Cl} + AgOH = AgCl + Hg{<}^{C_nH_{2n+1}}_{OH}$$

which yield salts with acids. All these compounds are extremely poisonous, especially when the vapours of the volatile ones are breathed. Strong dilution with air does not prevent this action, long breathing of such a mixture producing chronic poisoning of the most fearful description.

No compounds of mercury with alcohol radicals of the formula $Hg_2(C_nH_{2n+1})_2$, corresponding to mercurous chloride, have been obtained.

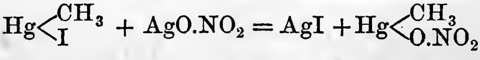
362. *Methyl Compounds.*—In order to prepare *mercury dimethyl* one per cent. sodium amalgam is slowly added with constant shaking to a mixture of methylic iodide with one-tenth of its volume of ethylic acetate. The mixture becomes hot, while mercury and sodic iodide separate. If the proportion of the latter becomes so large that the liquid becomes pulpy, all volatile matters must be distilled off and treated anew with sodium amalgam. This treatment is continued until one atom of sodium has been added for every molecule of methylic iodide, and a small quantity of the liquid no longer yields iodine on boiling with nitric acid. The distillate, after addition of water, is shaken with potassic hydrate to remove ethylic acetate, and the separated heavy oil dried by calcic chloride and rectified.

Mercury dimethyl, $Hg{<}^{CH_3}_{CH_3}$, is a colourless refractive liquid not miscible with water, boiling at 95°, and has sp. gr. 3·069 at ordinary temperatures. It has a faint, somewhat sweet odour, does not alter in air, is, however, readily inflammable, and burns with a luminous flame with evolution of mercury vapours. It dissolves caoutchouc, resin, and phosphorus.

Mercury methyl-iodide, $Hg{<}^{CH_3}_{I}$, is prepared from the preceding by addition of iodine to its aqueous solution. It separates in crystals, and is obtained pure on recrystallisation from hot alcohol in white nacreous plates. It melts at 143°, sublimes readily, is insoluble in water, but is readily soluble in alcohol and ether.

Mercury methyl-chloride, $Hg{<}^{CH_3}_{Cl}$, completely resembles the iodide.

An alcoholic solution of the iodide gives, on addition of argentic nitrate, a precipitate of argentic iodide, and the filtrate on evaporation in vacuo yields colourless, transparent prisms of *mercury methyl-nitrate :*



$$Hg{<}^{CH_3}_{I} + AgO.NO_2 = AgI + Hg{<}^{CH_3}_{O.NO_2}$$

readily soluble in water, but difficultly in alcohol. It melts at

100°, and on cooling becomes crystalline again. From its aqueous solution metallic chlorides precipitate mercury ethyl-chloride; alkalies produce no precipitate.

363. *Ethyl Compounds.—Mercury diethyl,* $Hg(C_2H_5)_2$, is prepared like the methyl compound, and shows similar properties. It is a liquid of sp. gr. 2·44 and boiling at 159°. The vapour density is 9·97. At 200° its vapour decomposes into mercury and butane.

Mercury ethyl-chloride, $Hg\!<\!\begin{matrix}C_2H_5\\ Cl\end{matrix}$, prepared, amongst other methods, by mixing solutions of mercury diethyl and mercuric chloride:

$$Hg(C_2H_5)_2 + HgCl_2 = 2Hg(C_2H_5)Cl,$$

forms white silvery needles.

Mercury ethyl-iodide, $Hg\!<\!\begin{matrix}C_2H_5\\ I\end{matrix}$, obtained from mercury and ethylic iodide in diffused daylight. By direct sunlight it is decomposed into mercury and butane (together with some ethane and ethylene).

By treatment of the haloid compounds with moist argentic oxide, *mercury ethyl-hydrate,* $Hg\!<\!\begin{matrix}C_2H_5\\ OH\end{matrix}$, goes into solution, and is left on evaporation as a strongly caustic alkaline liquid, which precipitates most metals from their salts as hydrates and yields crystalline salts with acids.

364. *Mercury dipropyl,* $Hg(CH_2.CH_2.CH_3)_2$, boils at 189°–191° and has sp. gr. 2·124 at 16°.

Mercury diisobutyl, $Hg(C_4H_9)_2$, distils between 205°–207°; sp. gr. 1·835 at 15°.

Mercury diisoamyl, $Hg(C_5H_{11})_2$, is readily obtained from a mixture of isoamylic iodide, acetic ether, and sodium amalgam. It is a colourless liquid, cannot be distilled unchanged, is insoluble in water, has sp. gr. 1·66, and gives with iodine crystalline plates of mercury isoamyl iodide, $Hg(C_5H_{11})I$.

Zinc Compounds of the Alcohol Radicals.

365. On submitting granulated zinc for a long time to the action of alkylic iodides with exposure to light, then, as with other metals, bodies of the formula $Zn(C_nH_{2n+1})I$ result. The same change occurs on heating, only goes further, so that in sealed tubes zinc and paraffins (as di-radicals) are formed (§ 150), some zinc compound of the alcohol radical being formed at the same time. The zinc compound is obtained in larger quantity when anhydrous ether is mixed with the alkylic iodide and the mixture heated with zinc in sealed tubes to 130°–150°.

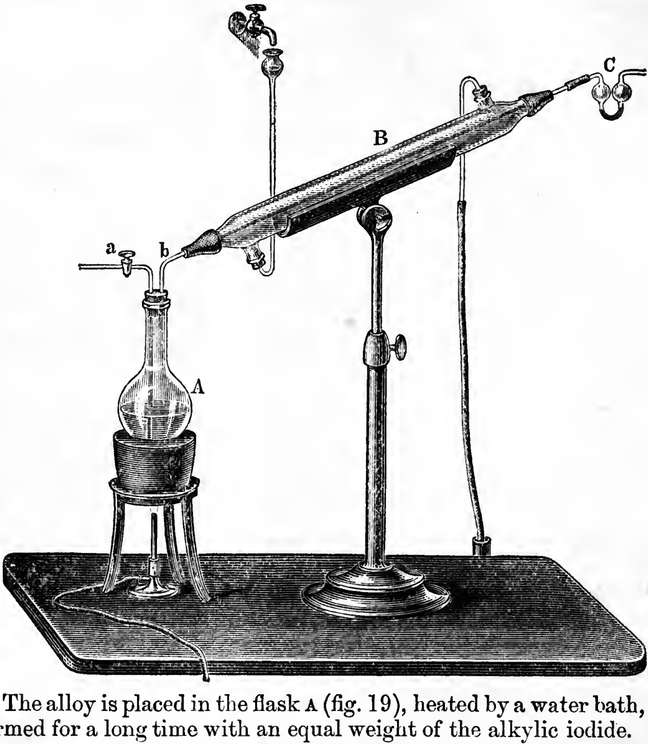
After cooling the tube is carefully opened, when gaseous products (paraffins, &c.) escape. By gentle warming the ether is expelled, and the residue, consisting mainly of the iodo-zinc compound, distilled in a stream of carbonic anhydride, decomposition occurring as shown by the equation:

$$2Zn(C_nH_{2n+1})I = ZnI_2 + Zn(C_nH_{2n+1})_2.$$

Organo-zinc compounds may also be obtained by heating the alkyl haloid with granulated zinc or zinc filings in presence of a small quantity of iodine, the apparatus employed resembling that next described.

The organo-zinc compounds are also obtained by employment of an alloy of zinc and sodium. To prepare this, zinc is heated in a Hessian crucible until it volatilises freely, and one-fourth of its weight of sodium stirred in. After the combination of the metals the crucible is removed from the fire, filled with dry sand to prevent contact with air, and then cooled. When cold, the crucible is broken, and any sodium adhering to the regulus cut off, and the last traces removed by treatment with water. The well-dried metallic mass is then coarsely powdered and preserved in well-stoppered glass vessels.

FIG. 19.



The alloy is placed in the flask A (fig. 19), heated by a water bath, and warmed for a long time with an equal weight of the alkylic iodide. The flask is connected with an inverted condenser B, in which the evolved vapours are condensed and flow back into the flask. The condenser tube has at its upper end a small set of bulbs C, in whose bend a small quantity of mercury prevents access of air whilst allowing the escape of any gas evolved. Previous to heating the ingredients the whole apparatus is filled with carbonic anhydride by means of the tapped tube *a*, and the tap then closed.

After completion of the reaction the flask is connected with a condenser placed in the usual way, whose lower end is connected with a receiver provided with a mercury valve similar to that above described. The zinc compound in the flask formed according to the equation:

$$ZnNa_2 + 2IC_nH_{2n+1} = 2NaI + Zn(C_nH_{2n+1})_2,$$

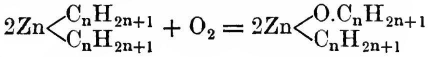
is then distilled, a current of dry carbonic anhydride passing through the tube *a*.

Finally, the organo-zinc compounds are obtained by heating the corresponding mercury compounds with zinc filings to 100°–130°. The separated mercury amalgamates with the excess of zinc:

$$Hg(C_nH_{2n+1})_2 + Zn_2 = HgZn + Zn(C_nH_{2n+1})_2.$$

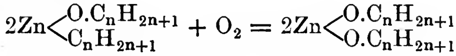
The product is then distilled in a stream of carbonic anhydride.

366. The zinc organo compounds are colourless, peculiarly smelling bodies, which oxidise in air with evolution of fumes and mostly with spontaneous inflammation. They burn with a bluish green flame and formation of thick fumes of zincic oxide. If the oxidation be moderated by allowing the ethereal solutions to remain in imperfectly closed vessels, two oxidation products are formed by the oxygen atoms placing themselves between the zinc and the alcohol radical—namely, first according to the equation:



$$2Zn{<}\begin{array}{l}C_nH_{2n+1}\\C_nH_{2n+1}\end{array} + O_2 = 2Zn{<}\begin{array}{l}O.C_nH_{2n+1}\\C_nH_{2n+1}\end{array}$$

and on further oxidation:



$$2Zn{<}\begin{array}{l}O.C_nH_{2n+1}\\C_nH_{2n+1}\end{array} + O_2 = 2Zn{<}\begin{array}{l}O.C_nH_{2n+1}\\O.C_nH_{2n+1}\end{array}$$

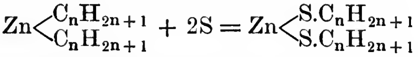
The latter compounds decompose on contact with water into alcohols and zincic hydrate:

$$Zn(O.C_nH_{2n+1})_2 + 2H_2O = Zn(OH)_2 + 2HO.C_nH_{2n+1}.$$

The unoxidised compounds also react on water with explosive violence, yielding paraffins (hydrides of the alcohol radicals) (§ 149):

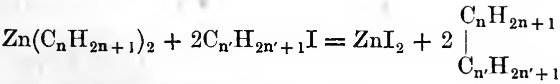
$$Zn(C_nH_{2n+1})_2 + 2HOH = Zn(OH)_2 + 2C_nH_{2n+2}.$$

Like oxygen, sulphur unites directly with them, forming zinc mercaptides:



$$Zn{<}\begin{array}{l}C_nH_{2n+1}\\C_nH_{2n+1}\end{array} + 2S = Zn{<}\begin{array}{l}S.C_nH_{2n+1}\\S.C_nH_{2n+1}\end{array}$$

With the haloid compounds of the alcohol radicals they give, especially on heating, zinc haloids and paraffins (di-radicals) (§ 150):



$$Zn(C_nH_{2n+1})_2 + 2C_{n'}H_{2n'+1}I = ZnI_2 + 2\begin{array}{l}C_nH_{2n+1}\\|\\C_{n'}H_{2n'+1}\end{array}$$

Free halogens yield, by a very violent reaction, zinc haloids and alkylic haloids:

$$Zn(C_nH_{2n+1})_2 + 2Br_2 = ZnBr_2 + 2C_nH_{2n+1}Br.$$

Their employment in the preparation of tertiary phosphines (§ 297) of organo-metallic bodies, and of tertiary alcohols (§ 163), has already been mentioned.

Ethereal solutions of these zinc compounds absorb sulphurous anhydride and nitric oxide gases with formation of crystalline salts of peculiar acids, of which the sulphur acids have already (§ 252) been noticed.

367. *Zinc methyl, zinc dimethyl,* $\mathrm{Zn}{<}\substack{CH_3\\CH_3}$, is usually prepared by heating mercury dimethyl with zinc, further by heating methylic iodide with zinc-sodium alloy or with powdered zinc in sealed glass tubes at 100°. It is a colourless, strongly refractive, extremely unpleasant smelling liquid, of sp. gr. 1·386 at 10·5°, which boils at 46°. Mixed with ethylic ether, it yields between 51° and 57° a liquid which cannot be separated by fractional distillation and whose proportional composition is represented by the formula $2Zn(CH_3)_2,(C_2H_5)_2O$.

On addition of some methylic alcohol to zinc methyl there is formed, according to the equation

$$\mathrm{Zn}{<}\substack{CH_3\\CH_3} + HO.CH_3 = CH_4 + \mathrm{Zn}{<}\substack{CH_3\\O.CH_3}$$

Zinc methyl-methylate as a white, spongy, somewhat crystalline mass. If excess of methylic alcohol be employed, solid zinc dimethylate is obtained. Zinc methyl inflames in air.

368. *Zinc ethyl, zinc diethyl,* $Zn(C_2H_5)_2$, completely resembles the methyl compound, has sp. gr. 1·182, boils at 118°, and has a vapour density of 4·26. In ethereal solution it absorbs two molecules of nitric oxide gas, and yields large colourless crystals, in which one-half of the ethyl is still united with zinc:

$$Zn(C_2H_5)_2 + N_2O_2 = C_2H_5.N_2O_2.(ZnC_2H_5).$$

The action of water causes ethane to be evolved, whilst the basic zinc salt of *dinitro-ethylic acid* results:

$$C_2H_5N_2O_2(ZnC_2H_5) + H_2O = C_2H_6 + C_2H_5N_2O_2(Zn.OH),$$

from whose solution one-half of the zinc can be precipitated by means of carbonic anhydride:

$$2C_2H_5.N_2O_2.Zn.OH + CO_2 = ZnCO_3 + H_2O + (C_2H_5N_2O_2)_2Zn.$$

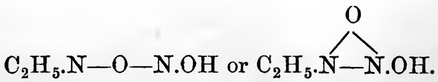
From the soluble neutral zinc salt, other salts of dinitro-ethylic acid can be prepared by double decomposition:

$$(C_2H_5N_2O_2)_2Zn + Na_2CO_3 = ZnCO_3 + 2C_2H_5N_2O_2.Na.$$

They are all difficultly crystallisable, and when heated in the dry state explode violently. By treatment of dinitro-ethylic acid or its salt with nascent hydrogen, equal molecules of ethylamine and ammonia are obtained:

$$C_2H_5N_2O_2H + 8H = C_2H_5.NH_2 + NH_3 + 2H_2O.$$

Therefore the constitution of the acid is best expressed by the formula



$$C_2H_5.N{-}O{-}N.OH \text{ or } C_2H_5.\overset{O}{\overbrace{N{-}N}}.OH.$$

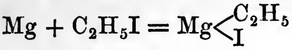
369. *Zinc dipropyl,* $Zn(CH_2.CH_2.CH_3)_2$, boils at 146° and is spontaneously inflammable.

Zinc diisobutyl, $Zn(C_4H_9)_2$, boils between 185° and 188°.

Zinc diisoamyl, $Zn(C_5H_{11})_2$, is liquid, has sp. gr. 1·022, boils at 220°, and fumes in the air without inflaming spontaneously.

OTHER METALLIC COMPOUNDS OF THE ALCOHOL RADICALS.

370. *Magnesium diethyl*, $Mg.(C_2H_5)_2$, is obtained as a volatile liquid, smelling like garlic, when magnesium filings are digested with ethylic iodide in absence of air. There is first formed solid magnesium ethyl iodide:



$$Mg + C_2H_5I = Mg\begin{cases}C_2H_5\\ I\end{cases}$$

which on strong heating in vessels filled with carbonic anhydride leaves a residue of magnesic iodide, whilst liquid magnesium diethyl distils over.

Magnesium diethyl inflames spontaneously in air, and is decomposed with explosive violence by water into magnesic hydrate and ethane. *Magnesium dimethyl* is entirely similar in preparation and properties.

371. Compounds of the *alkali metals* with the alcohol radicals cannot be obtained in the isolated state; they are undoubtedly formed by the action of sodium or potassium on organo-zinc compounds, zinc being separated even at ordinary temperatures:

$$Zn(C_2H_5)_2 + Na_2 = Zn + 2NaC_2H_5.$$

The resulting liquid crystallises at low temperatures, but invariably contains much unaltered zinc compound, and is at once converted by water into ethane, zincic hydrate, and sodic hydrate:

$$NaC_2H_5 + H_2O = NaOH + C_2H_6.$$

Sodium ethyl, when mixed with ethylic iodide, yields sodic iodide at ordinary temperatures, but does not give diethyl (butane), but a mixture of ethylene and ethane:

$$NaC_2H_5 + IC_2H_5 = NaI + C_2H_6 + C_2H_4.$$

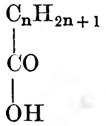
372. Compounds of thallium and tungsten with ethyl are also known, but the metals are not united by all their bonds to ethyl, but in part also to negative elements. Amongst such bodies are chloride, nitrate, and sulphate of the strongly positive monacid radical thallium diethyl, $Tl(C_2H_5)_2Cl$, $Tl(C_2H_5)_2.O.NO_2$, $[Tl(C_2H_5)_2]_2SO_4$, &c. Tungsten gives with methylic iodide tungsten trimethyl iodide, $W(CH_3)_3I$, crystallising in colourless tables.

DISUBSTITUTION PRODUCTS OF THE PARAFFINS.

Derivatives of the Diad Radicals, C_nH_{2n}.

373. The replacement of two of the hydrogen atoms of a paraffin by other elements yields compounds of the diad hydrocarbon nucleus C_nH_{2n}. It has already been pointed out (§ 143) that three different groups are thereby formed, which are named respectively after their simplest oxygen compounds.

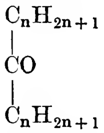
374. 1. *Aldehyde Derivatives.*—In these the substitution has taken place on a *single, terminal* carbon atom of the nucleus. The simplest oxides are the *aldehydes :*



$$\begin{array}{l} C_nH_{2n+1} \\ | \\ CO \\ | \\ OH \end{array}$$

the first oxidation products of the primary monacid alcohols (§ 160). The names of their hydrocarbon radicals, $C_nH_{2n+1}.CH$, are derived from those of the radicals C_nH_{2n+1} by addition of the terminal disyllable 'idene.' Thus from ethyl, $CH_3.CH_2$, there is formed ethyl-idene, $CH_3.CH$. The general name *alkyl-idenes* is applied to the whole group.

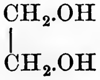
375. 2. *Ketone derivatives* result when both substitution positions are on one and the same *intermediate* carbon atom. The oxides



$$\begin{array}{l} C_nH_{2n+1} \\ | \\ CO \\ | \\ C_nH_{2n+1} \end{array}$$

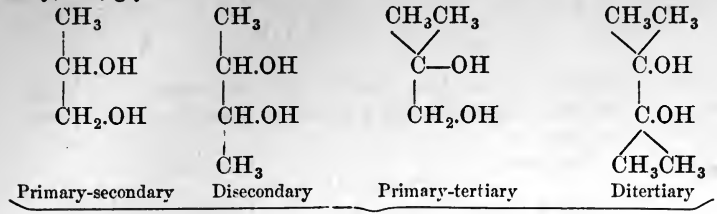
are termed *ketones*, and are formed by oxidation of secondary alcohols (§ 160).

376. 3. *Glycol derivatives* are obtained by substitution of hydrogen atoms united to different carbon atoms. In the *glycols* or diacid alcohols they are replaced by OH. The first member of the series is a dicarbonide :



$$\begin{array}{l} CH_2.OH \\ | \\ CH_2.OH \end{array}$$

a diprimary alcohol. With greater carbon contents there occur in addition also primary-secondary, disecondary, primary-tertiary, ditertiary, &c., glycols:



Glycols.

If the substitution positions are on neighbouring carbon atoms the free radicals can—by double union of the two carbon atoms—occur as free molecules. These are the hydrocarbons of the formula C_nH_{2n}, whose names are derived from those of the alcohol radicals by affixing the terminal syllable 'ene;' as $CH_2:CH_2$, ethylene; $CH_3.CH:CH_2$, propylene, &c.

377. In all three categories the diad radicals, C_nH_{2n}, can be united with two dissimilar monad elements or radicals. There thereby result complications which do not occur in the compounds of the monad alcohol radicals. There is, for instance, a chloro-hydrate, $C_2H_4.Cl(OH)$, between the chloride, $C_2H_4Cl_2$, and the hydrate, $C_2H_4(OH)_2$. Notwithstanding the numerous theoretical possibilities, the number of compounds of the diad radicals, C_nH_{2n}, actually known, is far smaller than that of the alcohol radical compounds.

ALDEHYDE DERIVATIVES.

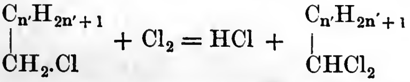
Compounds of the Alkylidene Radicals, $C_nH_{2n+1}.CH:$.

378. In the aldehyde derivatives two of the hydrogen atoms of a single primarily united carbon atom of a paraffin have been replaced by other elements or compound radicals.

Halogen Compounds of the Aldehyde Radicals.

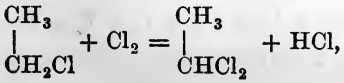
379. Of the halogen compounds of the aldehyde radicals several chlorides, $C_mH_{2m+1}.CHCl_2$, and bromides are known, but only a single iodide.

The chlorine compounds can be prepared directly from the paraffins and their primary monochlor derivatives. The replacement of a second atom of hydrogen by chlorine occurs mainly in the immediate neighbourhood of the chlorine atom originally present:



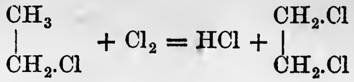
$$\begin{matrix} C_{n'}H_{2n'+1} \\ | \\ CH_2.Cl \end{matrix} + Cl_2 = HCl + \begin{matrix} C_{n'}H_{2n'+1} \\ | \\ CHCl_2 \end{matrix}$$

but other products—especially olefine dichlorides—are always formed. In working with ethylic chloride, for instance, the reaction occurs to a much greater extent according to the equation:



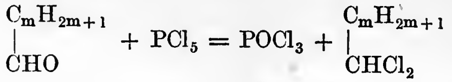
$$\begin{matrix} CH_3 \\ | \\ CH_2Cl \end{matrix} + Cl_2 = \begin{matrix} CH_3 \\ | \\ CHCl_2 \end{matrix} + HCl,$$

than according to the equation:



$$\begin{array}{l} CH_3 \\ | \\ CH_2.Cl \end{array} + Cl_2 = HCl + \begin{array}{l} CH_2.Cl \\ | \\ CH_2.Cl \end{array}$$

Another method of preparation of these compounds consists in bringing the respective aldehydes into reaction with phosphoric pentachloride:



$$\begin{array}{l} C_mH_{2m+1} \\ | \\ CHO \end{array} + PCl_5 = POCl_3 + \begin{array}{l} C_mH_{2m+1} \\ | \\ CHCl_2 \end{array}$$

and separating the products by fractional distillation or by converting the phosphoric oxychloride into phosphoric acid by addition of water, separating the oily chloride from the aqueous solution, and rectifying it alone.

380. *Methene Haloids.—Methene dichloride*, CH_2Cl_2, is formed by the action of chlorine on methylic chloride:

$$CH_3Cl + Cl_2 = HCl + CH_2Cl_2,$$

and is therefore the second chlorine substitution product of methane, *dichlor methane*. It is more commonly prepared by placing methylic iodide in a retort, covering with water, and then passing chlorine through the tubulus into the liquid. The very volatile methene dichloride collects in the receiver, which must be kept well cooled, whilst iodine is left in the retort:

$$2CH_3I + 3Cl_2 = 2CH_2Cl_2 + I_2 + 2HCl.$$

After drying over calcic chloride and rectifying, methene dichloride is a colourless liquid of sweet, penetrating odour, nearly insoluble in water, boiling at 41°, and having sp. gr. 1·344.

The same method may be applied to the formation of *methene dibromide*, according to the equation:

$$2CH_3I + 3Br_2 = 2CH_2Br_2 + 2HBr + I_2.$$

It forms a heavy liquid, boiling at 80°–82° and of sp. gr. 2·084 at 11·5°.

Methene diiodide, CH_2I_2, is a colourless, sweet-smelling oil of sp. gr. 3·345, which boils at 182° and solidifies in the cold to brilliant leafy crystals, melting at + 6°. The vapour density is 9·55. It is insoluble in water and will not moisten glass.

It is obtained by distilling iodoform with an alcoholic solution of potassic hydrate, the alcohol being converted into various oxidation products by the oxygen evolved:

$$CHI_3 + KOH + KI + CH_2I_2 + O;$$

also by heating iodoform for several hours with the most concentrated aqueous hydriodic acid at 125°–150°:

$$CHI_3 + HI = CH_2I_2 + I_2;$$

by heating chloroform with hydriodic acid:

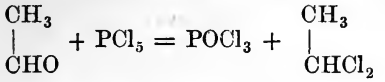
$$CHCl_3 + 4HI + CH_2I_2 + I_2 + 3HCl;$$

(compare § 149); or by heating iodoform alone in sealed tubes to 150°, when much methene diiodide is formed in addition to other products not yet investigated.

381. *Ethylidene Haloid Compounds.—Ethylidene dichloride :*

$$C_2H_4Cl_2 \text{ or } CH_3.CHCl_2,$$

is obtained by the action of chlorine gas when exposed to light on ethylic chloride, together with ethylene dichloride and further substitution products (§ 377), from which it must be separated by fractional distillation. It is also formed by the action of phosphoric chloride on ethylic aldehyde :



$$\begin{array}{l}CH_3\\ |\\ CHO\end{array} + PCl_5 = POCl_3 + \begin{array}{l}CH_3\\ |\\ CHCl_2\end{array}$$

and is a colourless liquid of chloroform-like odour, 1·198 sp. gr., and 58°–59° boiling point, which is insoluble in water.

Ethylidene dibromide, $CH_3.CHBr_2$, is formed by conducting the vapour of ethylic aldehyde into phosphoric bromide, a liquid being obtained which contains ethylidene dibromide and phosphoric oxybromide; on addition of ice the latter is converted into phosphoric acid and hydrobromic acid, from which the ethylidene dibromide separates as a yellowish oil. It is also obtained by the action of bromine upon ethylic bromide :

$$CH_3.CH_2Br + Br_2 = CH_3.CHBr_2 + HBr,$$

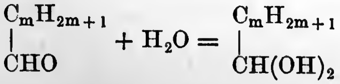
and is separated from other products formed at the same time by fractional distillation. It boils at 114°. It is very readily decomposed, water on gentle heating yielding with it hydrobromic acid and probably aldehyde.

382. *Propylidene dichloride*, $CH_3.CH_2.CHCl_2$, obtained from propylic aldehyde and phosphoric chloride, is a liquid boiling at 84°–87°, of onion-like odour.

Isoamylidene dichloride, $(CH_3)_2CH.CH_2.CHCl_2$, is obtained from isoamylic aldehyde, by means of phosphoric chloride, as an oil boiling at 130° and of sp. gr. 1·05 at 24°.

Oxygen Compounds of the Aldehyde Radicals.

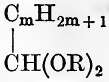
383. As already mentioned, the anhydrous oxides of the aldehyde radicals are termed aldehydes. The dihydrates, $\begin{array}{l}C_mH_{2m+1}\\ |\\ CH(OH)_2\end{array}$, corresponding to these oxides, $\begin{array}{l}C_mH_{2m+1}\\ |\\ CHO\end{array}$, cannot be obtained in a state of purity, although they probably exist in aqueous solution. On mixing an aldehyde with water, heat is generally evolved and a diminution of volume observed, probably in consequence of union with the elements of water :



$$\begin{array}{l}C_mH_{2m+1}\\ |\\ CHO\end{array} + H_2O = \begin{array}{l}C_mH_{2m+1}\\ |\\ CH(OH)_2\end{array}$$

Nevertheless by mere distillation these hydrates dissociate into water and aldehyde. It appears that the grouping of several hydroxyl groups round a single carbon atom is invariably accompanied with but small intensity of union and with a strong tendency to decompose into water and anhydride. But these polyhydrates become much more stable when carbon groups rich in negative elements are in combination also. If ethyl aldehyde, $CH_3.CHO$, be converted into chloral, $CCl_3.CHO$, the latter yields with water chloral hydrate, $CCl_3.CH(OH)_2$, a very stable body.

As two oxynuclei can be united at the same time to an aldehyde radical, oxides and salts occur of the general formula :

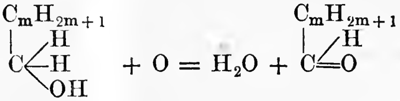


$$\begin{array}{l} C_mH_{2m+1} \\ | \\ CH(OR)_2 \end{array}$$

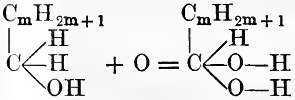
in which R is the radical either of an alcohol or an acid.

The Aldehydes.

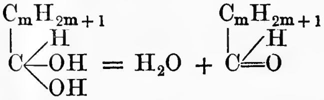
384. The aldehydes are generally prepared by the moderated action of ozone or oxidising agents upon primary alcohols or their ethers. One atom of oxygen then removes from the primary alcohol two atoms of hydrogen in the form of water (therefore the name aldehyde, abbreviated from *alcohol dehydrogenatum*). One of these hydrogen atoms is from the hydroxyl group, the second from one of the hydrogen atoms united to the same carbon atom :



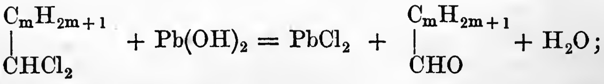
More probably the first action is the direct union of the oxygen so as to form a second hydroxyl group :



which then decomposes into water and aldehyde :

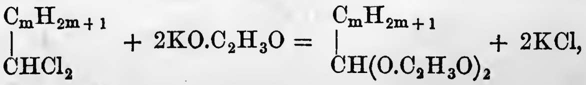


385. The aldehydes can be obtained from the haloid compounds of their radicals either directly by boiling with plumbic hydrate:



$$\begin{array}{l} C_mH_{2m+1} \\ | \\ CHCl_2 \end{array} + Pb(OH)_2 = PbCl_2 + \begin{array}{l} C_mH_{2m+1} \\ | \\ CHO \end{array} + H_2O;$$

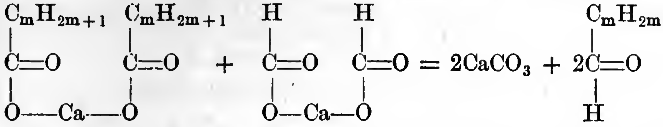
or by first converting into the acetate by means of potassic acetate :



$$\begin{array}{l} C_mH_{2m+1} \\ | \\ CHCl_2 \end{array} + 2KO.C_2H_3O = \begin{array}{l} C_mH_{2m+1} \\ | \\ CH(O.C_2H_3O)_2 \end{array} + 2KCl,$$

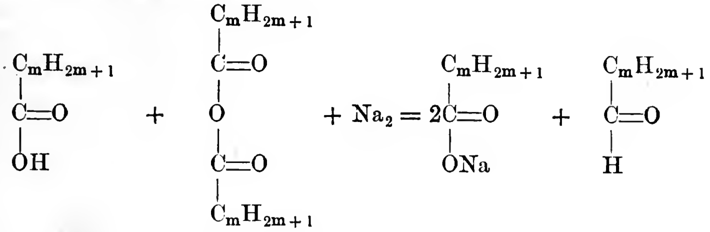
and then saponifying. In this latter decomposition the alkali must not be employed in excess, as it very readily converts the aldehydes into resinous products, whose nature has not yet been sufficiently made out.

386. A further method for the formation of the aldehydes of general application, is from those acids which the aldehydes themselves yield when oxidised. If the calcic salt of such an acid be intimately mixed with calcic formate and the mixture submitted to dry distillation, calcic carbonate remains behind, whilst the aldehyde distils over: 7



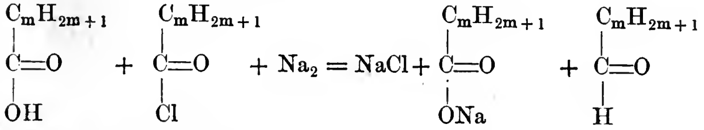
$$\begin{array}{ccccccccc} C_mH_{2m+1} & C_mH_{2m+1} & & H & H & & & & C_mH_{2m+1} \\ | & | & & | & | & & & & | \\ C{=}O & C{=}O & + & C{=}O & C{=}O & = & 2CaCO_3 & + & 2C{=}O \\ | & | & & | & | & & & & | \\ O\text{—}Ca & \text{—}O & & O\text{—}Ca & \text{—}O & & & & H \end{array}$$

The aldehydes appear also to be formed without exception by the action of sodium amalgam upon a mixture of the acid with the acid anhydride or acid chloride. These decompositions probably occur as in the following equations:



$$\begin{array}{ccccccc} & & C_mH_{2m+1} & & & & \\ & & | & & & & \\ C_mH_{2m+1} & & C{=}O & & C_mH_{2m+1} & & C_mH_{2m+1} \\ | & & | & & | & & | \\ C{=}O & + & O & + Na_2 = & 2C{=}O & + & C{=}O \\ | & & | & & | & & | \\ OH & & C{=}O & & ONa & & H \\ & & | & & & & \\ & & C_mH_{2m+1} & & & & \end{array}$$

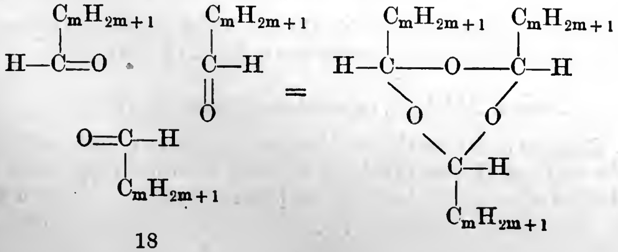
Acid anhydride.



$$\begin{array}{ccccccc} C_mH_{2m+1} & & C_mH_{2m+1} & & C_mH_{2m+1} & & C_mH_{2m+1} \\ | & & | & & | & & | \\ C{=}O & + & C{=}O & + Na_2 = NaCl + & C{=}O & + & C{=}O \\ | & & | & & | & & | \\ OH & & Cl & & ONa & & H \end{array}$$

Acid chloride.

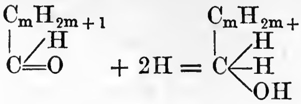
387. The aldehydes are generally characterised by the ease of their conversion into polymeric modifications, especially yielding tripled molecules. Their formation may be explained on the supposition that the oxygen atoms of the aldehydes unite on polymerisation to the carbon atoms of two molecules, thereby joining the molecules together. This may be shown by the formula:



On heating to higher temperatures these polymerised aldehydes split up again into the simple molecules.

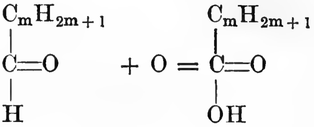
388. The aldehydes, as the compounds intermediate between the primary alcohols and acids, can readily be converted into either.

By treatment with nascent hydrogen—by sufficiently energetic action of sodium amalgam upon a slightly acidulated aqueous solution of aldehyde—two atoms of hydrogen are combined, and the primary alcohol regenerated, from which the aldehyde can be obtained by oxidation:



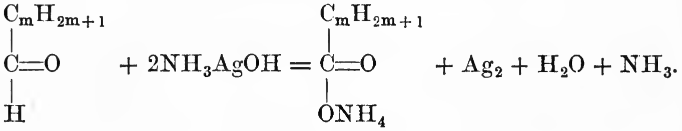
$$\begin{array}{l} C_mH_{2m+1} \\ |\;\diagup H \\ C{=}O \end{array} + 2H = \begin{array}{l} C_mH_{2m+1} \\ |\;\;\; H \\ C{<}H \\ \;\;\; OH \end{array}$$

The aldehydes are slowly converted into acids by mere exposure to atmospheric oxygen, and this change occurs considerably more quickly with oxidising agents:



$$\begin{array}{l} C_mH_{2m+1} \\ | \\ C{=}O \\ | \\ H \end{array} + O = \begin{array}{l} C_mH_{2m+1} \\ | \\ C{=}O \\ | \\ OH \end{array}$$

The action of argentic oxide is especially characteristic. By adding ammonia to argentic nitrate until the argentic oxide first precipitated is redissolved, a liquid is obtained which, when added to aldehyde at ordinary temperatures, but more quickly on warming, gives a deposit of metallic silver, whilst the ammonic salt of the acid remains in solution:



$$\begin{array}{l} C_mH_{2m+1} \\ | \\ C{=}O \\ | \\ H \end{array} + 2NH_3AgOH = \begin{array}{l} C_mH_{2m+1} \\ | \\ C{=}O \\ | \\ ONH_4 \end{array} + Ag_2 + H_2O + NH_3.$$

If the aldehyde is miscible with water the silver separates in great part as a coherent, mirror-like film on the sides of the vessel. If an aldehyde be brought into contact with freshly precipitated argentic oxide, the argentic salt of the acid is formed:

$$C_mH_{2m+1}.CO.H + 3AgOH = C_mH_{2m+1}.CO.OAg + Ag_2 + 2H_2O.$$

In detecting or purifying aldehydes use is made of their combinations with the alkaline hydric sulphites and with ammonia (see later).

By action of phosphoric chloride the aldehydes and their polymers are converted into the dichlorides of the radicals (§ 379).

Formic Aldehyde, or Methene Oxide, CH_2O.

389. *Methene oxide, methylic aldehyde,* also known (as the aldehyde of formic acid) as *formic aldehyde,* is only known in the state of vapour and in aqueous solution, which probably contains it as a dihydrate. In absence of water it polymerises with great readiness.

The aqueous solution of formic aldehyde is most readily obtained by oxidation of methylic alcohol. For this purpose some methylic alcohol is placed on the bottom of a tri-tubulated Woulff's bottle. In one of the side necks a glass tube open at both ends is placed so as to dip into the methylic alcohol, whilst the other is connected with a condenser, this with a receiver, and this latter attached air-tight to a powerful aspirator. The condenser is filled with ice-cold water, with which the receiver is also surrounded. When the aspirator has been set working, the middle neck of the Woulff's bottle is closed with a stopper, from which hangs a spiral of platinum wire which has been heated to glowing. A powerful stream of air is now drawn through the open tube, which bubbling through the methylic alcohol becomes charged with its vapour. The hot platinum wire causes the oxidation of the vapour, sufficient heat being thereby evolved to keep the wire at the necessary temperature. The resulting formic aldehyde, together with water and unaltered methylic alcohol, liquefy in the condenser and collect in the receiver.

The distillate has a penetrating smell, reduces solutions of silver salts, and is converted into a yellow oil by potassic hydrate. Formic aldehyde has not yet been obtained from it in a pure state.

If the liquid be evaporated on the water bath the greater part of the aldehyde is evolved. A part, however, remains as a solid mass of paramethyl aldehyde.

390. *Paramethyl aldehyde*, or *trimethene oxide*, formerly known as dioxy-methylene, $C_3H_6O_3$, can be obtained in the following ways, in addition to the one given above :—

It is obtained directly from methene diiodide by heating with argentic oxalate. This latter must be mixed with twice its weight of powdered glass in order to moderate the reaction :

$$3CH_2I_2 + 3Ag_2C_2O_4 = 6AgI + 3CO_2 + 3CO + C_3H_6O_3.$$

In well-cooled condensers paramethyl aldehyde separates from the stream of gases in the solid state.

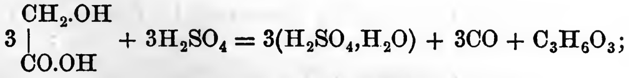
On heating methene diiodide with argentic acetate and acetic acid, *methene diacetate*, boiling at 170°, is formed :

$$CH_2I_2 + 2AgO.C_2H_3O = 2AgI + CH_2(OC_2H_3O)_2;$$

from which, by heating with water at 100° in sealed tubes, paramethyl aldehyde is obtained :

$$3CH_2(O.C_2H_3O)_2 + 3H_2O = 6HO.C_2H_3O + C_3H_6O_3.$$

It is obtained most readily by heating glycollic acid with concentrated sulphuric acid in a retort to 150° :



$$3\begin{array}{l}CH_2.OH\\ |\\ CO.OH\end{array} + 3H_2SO_4 = 3(H_2SO_4,H_2O) + 3CO + C_3H_6O_3;$$

paramethyl aldehyde condenses on the neck of the retort.

Paramethyl aldehyde is a colourless, indistinctly crystalline body, insoluble in water, alcohol, and ether. Though itself odourless it gives the penetrating odour of formic aldehyde when heated. It sublimes freely at 100°, melts at 152°, and boils at a slightly higher temperature. The vapour evolved is not paramethyl aldehyde, but the simple formic aldehyde. On cooling it polymerises again. The vapour density is found to be 1·037, which corresponds to the formula CH_2O.

That paramethyl aldehyde is correctly represented by the formula $C_3H_6O_3$ can only be inferred from its analogy with parathio-methyl aldehyde, into which it is readily converted by hydric sulphide, and which has been shown to possess the formula $C_3H_6S_3$.

If paramethyl aldehyde be heated with much water to 130°–150° in sealed tubes it dissolves, and the liquid then possesses the properties of a solution of formic aldehyde. In presence of water, therefore, the change into the polymeric modification does not occur, probably in consequence of the solution containing not CH_2O, but the dihydrate $CH_2(OH)_2$.

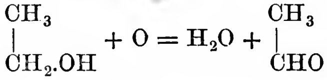
Baric hydrate solution, on boiling, colours paramethyl aldehyde yellow, and the liquid then contains some baric formate.

By careful addition of argentic oxide the aqueous solution of formic aldehyde is converted into formic acid:

$$CH_2O + 2AgOH = Ag_2 + CHO.OH + H_2O.$$

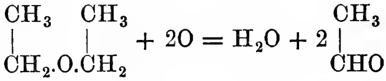
Acetic Aldehyde, or Ethylidene Oxide, C_2H_4O.

391. *Acetic aldehyde, ethylic aldehyde,* or simply *aldehyde,* is the first oxidation product of ethylic alcohol:



$$\begin{array}{l}CH_3\\ |\\ CH_2.OH\end{array} + O = H_2O + \begin{array}{l}CH_3\\ |\\ CHO\end{array}$$

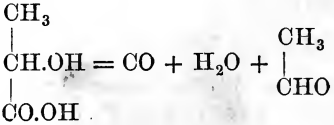
and ethylic ether



$$\begin{array}{l}CH_3 \quad CH_3\\ | \qquad\quad |\\ CH_2.O.CH_2\end{array} + 2O = H_2O + 2\begin{array}{l}CH_3\\ |\\ CHO\end{array}$$

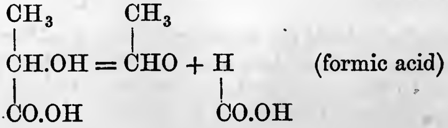
and is also formed in smaller quantity in the oxidation of many other bodies, such as albumen, sugars, fermentation lactic acid, &c.

From fermentation lactic acid it is also obtained, together with other products, by dry distillation:



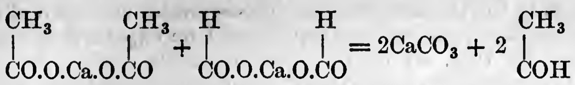
$$\begin{array}{l}CH_3\\ |\\ CH.OH\\ |\\ CO.OH\end{array} = CO + H_2O + \begin{array}{l}CH_3\\ |\\ CHO\end{array}$$

in larger quantity, together with formic acid, by heating with moderately concentrated sulphuric acid to 150° in sealed tubes:



$$\begin{array}{l}CH_3\\ |\\ CH.OH\\ |\\ CO.OH\end{array} = \begin{array}{l}CH_3\\ |\\ CHO\end{array} + \begin{array}{l}H\\ |\\ CO.OH\end{array} \qquad \text{(formic acid)}$$

Much aldehyde is also obtained by dry distillation of an intimate mixture of calcic acetate and formate:



$$\begin{array}{ccccc} CH_3 \qquad\qquad CH_3 & & H \qquad\qquad H & & CH_3 \\ | \qquad\qquad\quad | & + & | \qquad\qquad\quad | & = 2CaCO_3 + 2 & | \\ CO.O.Ca.O.CO & & CO.O.Ca.O.CO & & COH \end{array}$$

392. To prepare aldehyde two parts of 80 % alcohol are heated with three parts of manganic dioxide and a mixture of three parts of sulphuric acid and two parts of water, and the vapours condensed by strong cooling. The crude distillate, which contains several other bodies, such as acetal, ethylic acetate, water, and unaltered alcohol, is, in order to purify the aldehyde, mixed with ether, and the liquid saturated with dry ammonia gas. Aldehyde ammonia, insoluble in ether, is thereby separated:

$$CH_3.CHO + NH_3 = CH_3.CH(OH).NH_2,$$

in crystals, whilst all impurities remain in solution. The crystals, after washing with ether and drying over sulphuric acid, are dissolved in a little water, mixed with dilute sulphuric acid, and distilled, when aldehyde and some water pass over:

$$2CH_3.CH(OH).NH_2 + H_2SO_4 = (NH_4)_2SO_4 + 2CH_3.CHO.$$

The distillate is allowed to stand some time over fused calcic chloride and then rectified, the pure aldehyde being collected in receivers cooled with iced water.

Instead of manganic dioxide, potassic dichromate, in pieces about the size of peas, is generally used as the oxidising agent. Fifteen parts of this is treated with a mixture of ten parts of alcohol and twenty parts of sulphuric acid, which has been previously diluted with three times its volume of water.

The reaction, which speedily begins, is so violent that the liquid enters into ebullition. As the accompanying bodies are more difficultly volatile than aldehyde, it is usual to separate them from the latter by partial condensation before condensing it by strong cooling.

For this purpose the reaction vessel A (fig. 20), whose volume must be four times that of the mixed ingredients, is connected with the lower end of a glass worm B which is surrounded with water of 60°. In this the main portion of the accompanying vapours are condensed and returned into the retort A. The aldehyde vapours are conducted from the upper end of the worm tube into two cylinders C, C, containing anhydrous ether, and surrounded by a mixture of ice and salt, in which the aldehyde liquefies. At the end of the reaction, which is completed by slight heating of the reaction vessel by hot water, all the aldehyde is found mixed with ether in the two cylinders. Dry ammonia gas is now passed into the cylinders, and the crystalline aldehyde ammonia treated as already described to obtain pure aldehyde.

393. Acetic aldehyde is a mobile liquid boiling at 21°, of sp. gr. ·801 at 0°. In the air it evaporates with great celerity and large absorption of heat. The odour is peculiar, and when strongly diluted not unpleasant. The vapour, when breathed in large quantity, produces a feeling of tightness in the chest.

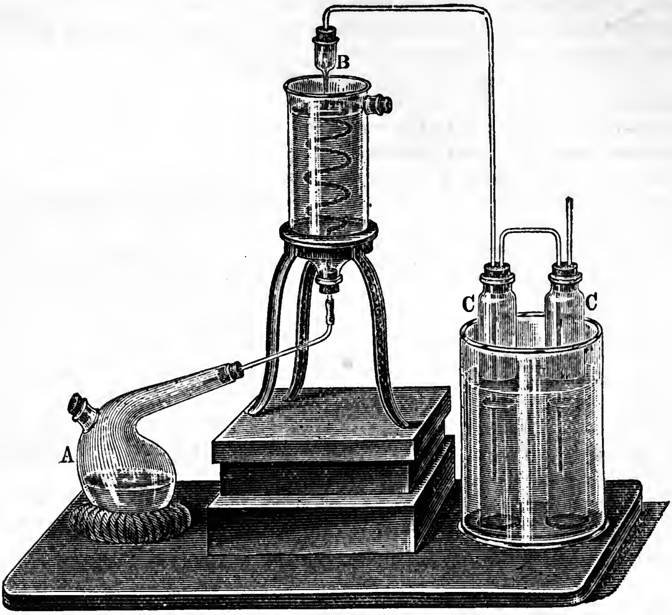
The vapour density is 1·52.

Acetic aldehyde mixes in every proportion with water, alcohol, and ether, in the two first cases with considerable evolution of heat.

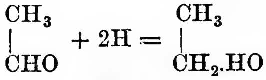
Aqueous aldehyde becomes rapidly acid on exposure to air, being converted by that, as by all other oxidising agents, into acetic acid. It precipitates metallic silver from ammoniacal silver solutions, ammonic acetate being formed :

$$CH_3.CHO + 2NH_3AgOH = Ag_2 + NH_3 + H_2O + CH_3.CO.O.NH_4.$$

FIG. 20.



By treatment of the slightly acidulated aqueous solution with sodium amalgam aldehyde is reconverted into ethylic alcohol :



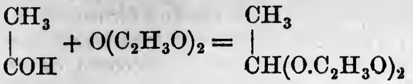
$$\begin{matrix} CH_3 \\ | \\ CHO \end{matrix} + 2H = \begin{matrix} CH_3 \\ | \\ CH_2.HO \end{matrix}$$

but some other products are formed at the same time, especially β-butylene glycol.

Phosphoric chloride converts acetic aldehyde into ethylidene dichloride (§ 381), and alkalies form from it a yellow resin (aldehyde resin) of still uncertain composition.

By long contact with aqueous hydrochloric acid aldehyde is converted into *aldol*; by heating with a little zincic chloride two molecules of aldehyde condense, with elimination of a molecule of water, into *crotonic aldehyde.*

By long heating at 180° with acetic anhydride in sealed glass tubes aldehyde is converted into *ethylidene acetate:*



$$\begin{array}{l}CH_3\\|\\COH\end{array} + O(C_2H_3O)_2 = \begin{array}{l}CH_3\\|\\CH(O.C_2H_3O)_2\end{array}$$

This is a colourless liquid, boiling at 169° and not miscible with water, but which on heating therewith yields aldehyde and two molecules of acetic acid.

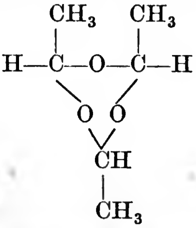
Further decompositions of ethylidene oxide will be mentioned later.

394. Chemically pure aldehyde remains quite unaltered in air-tight vessels. Small quantities of acids or of certain salts (as zincic chloride) cause its transformation on standing into two polymeric modifications, *paraldehyde* and *metaldehyde.*

At ordinary temperatures paraldehyde, triethylidene trioxide, $C_6H_{12}O_3$, is formed, and most quickly, and with great evolution of heat and diminution of volume, when a drop of strong sulphuric acid is added to pure aldehyde. Zincic chloride, sulphurous anhydride, and hydrochloric acid similarly cause this change in a short time. In order to obtain pure paraldehyde the modified aldehyde is cooled by a freezing mixture, and the crystals formed are separated from the portion remaining liquid, which still contains unchanged aldehyde.

Paraldehyde is a crystalline solid below +10°, and melts, when perfectly pure, at 10·5°. At 15° the liquid has the sp. gr. ·998; it boils at 124°. The vapour density is 4·58, being three times as great as that of aldehyde.

Paraldehyde is difficultly soluble in water, and still less on heating than at ordinary temperatures. By strongly superheating its vapour, and then condensing, ordinary aldehyde is obtained. The same decomposition occurs on distillation with sulphuric acid. Phosphoric chloride converts it completely into ethylidene chloride; acetic anhydride, on heating, into ethylidene acetate. By these reactions there is no doubt that the combination of three aldehyde molecules to one molecule of paraldehyde takes place according to the formula:



395. *Metaldehyde* is formed by the action of somewhat dilute sulphuric acid, sulphurous acid, calcic chloride, &c., at temperatures below 0°, and separates in white needles or prisms. Sometimes this modification is also obtained at ordinary temperatures under conditions still unascertained, but there is invariably only a small portion of the aldehyde transformed into metaldehyde. From the portion remaining liquid it is separated by decantation and suction. It is insoluble in water, difficultly soluble in cold alcohol, ether, carbonic disulphide, &c.

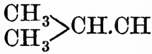
It sublimes slowly at 100°, more quickly and without fusion at 112°–115°. At the latter temperature it is partly converted into aldehyde, the conversion being complete on heating for several hours in a sealed tube. Phosphoric chloride converts it into ethylidene chloride. Its vapour density cannot be determined on account of its ready conversion into C_2H_4O, and on this account the molecular weight of metaldehyde remains unknown. It probably contains more than three aldehyde molecules united together in similar manner to that in paraldehyde.

Higher Aldehydes.

396. *Propionic aldehyde*, or *propylidene oxide*, $CH_3.CH_2.CHO$, is prepared by oxidation of primary propylic alcohol and by dry distillation of a mixture of calcic propionate and formate. It is a mobile liquid, of suffocating aldehyde-like odour, of sp. gr. ·8074 at 21°, and boils at 48·8°–49·5°. It is no longer miscible in every proportion with water, but requires five volumes of the latter for solution.

397. *Butyric aldehydes*, C_4H_8O. Two isomers exist corresponding to the two primary butylic alcohols.

Normal butyric aldehyde, or *butylidene oxide*, $CH_3.CH_2.CH_2.CHO$, is obtained by dry distillation of calcic normal butyrate and formate as a liquid of penetrating aldehydic odour. It boils at 75°, has sp. gr. ·834 at 0°, and dissolves in about twenty-seven parts of water. It is also formed in small quantity in the oxidation of albuminoids by manganic dioxide and sulphuric acid.

Isobutyric aldehyde, or *isobutylidene oxide*,  $\begin{matrix}CH_3\\CH_3\end{matrix}\!>CH.CHO$, is prepared by oxidation of ten parts of isobutylic alcohol by nine and a half parts of potassic bichromate and a mixture of nine parts of sulphuric acid with seventy-five parts of water. The reaction must be started by gentle heating, and then completes itself. The crude distillate must be fractioned, and the portion passing over between 60° and 80° shaken with a concentrated solution of hydric sodic sulphite. A compound of this latter with the aldehyde separates, which is pressed and distilled with solution of sodic hydrate, when pure isobutyric aldehyde is obtained. It is also prepared by the dry distillation of calcic isobutyrate and formate.

Isobutyric aldehyde is a colourless, strongly refractive liquid of penetrating odour, which boils at 61°–62° and has sp. gr. ·8226 at 0°. It dissolves at 20° in about nine times its weight of water.

By hydrochloric acid, or somewhat concentrated sulphuric acid, as also by addition of chlorine or bromine, isobutyric aldehyde polymerises with evolution of heat into

Paraisobutyric aldehyde, which crystallises in silky needles, recrystallisable from water and alcohol, and melts at 59°–60°. The boiling point is 194°, the found vapour density 7·256, which corresponds to the tripled molecule $C_{12}H_{24}O_3$, whose theoretical vapour density would be 7·464. At 200° paraisobutyric aldehyde is still not reconverted into isobutyric aldehyde.

398. *Valeric aldehydes*, $C_5H_{10}O$. Four of these bodies are possible, corresponding to the primary amylic alcohols; only two, however, are known as yet.

Normal valeric aldehyde, amylidene oxide:

$$CH_3.CH_2.CH_2.CH_2.CHO,$$

is obtained by dry distillation of normal calcic valerate with calcic formate as a liquid boiling at about 102° and requiring more than thirty parts of water for solution. Its odour is very similar to that of the following compound.

Isovaleric aldehyde, isoamylidene oxide, or *valeral:*

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH.CH_2.CHO,$$

is readily obtained from fermentation amylic alcohol. A lukewarm saturated solution of twelve parts of potassic dichromate is placed in a retort, and a mixture of sixteen parts of sulphuric acid with eleven parts of isoamylic alcohol and sixteen parts of water allowed to flow in slowly through a funnel tube. The temperature rapidly increases to that of distillation, and no external source of heat is required till nearly the end of the reaction. The vapours passing over are condensed in well-cooled receivers, and yield a distillate containing besides valeral some isoamylic alcohol, isovaleric acid, isoamylic isovalerate, and much water. Potassic hydrate is added to the distillate until alkaline, with shaking, in order to convert the acid into the potassic salt. The oil collected above the aqueous liquid is then poured off and shaken for a long time with a concentrated solution of hydric sodic sulphite. This latter combines with the valeral to a difficultly soluble compound, which separates in brilliant plates. These are collected on linen, pressed, washed with ether, dried, and distilled with concentrated solution of sodic hydrate, whereby valeral is regenerated.

Isovaleric aldehyde is a colourless liquid of suffocating apple-like odour, which boils at 92·5° and at 0° has sp. gr. ·822. By oxidising agents it is converted into isovaleric acid.

399. *Normal caproic aldehyde,* $CH_3.CH_2.CH_2.CH_2.CH_2.CHO$, is obtained by the dry distillation of a mixture of calcic normal caproate and formate. It forms a colourless liquid boiling at 127·9° and of sp. gr. ·8498 at 0°.

Another *caproic aldehyde,* probably $(CH_3)_2:CH.CH_2.OH$, is prepared by distillation of calcic isocaproate and formate as a penetrating but not unpleasant-smelling liquid, boiling at 121°. It yields with nascent hydrogen a hexylic alcohol boiling at 150°.

400. *Œnanthol,* or *œnanthic aldehyde,* $C_7H_{14}O$, is obtained by dry distillation of castor oil, the distillate being shaken with hydric sodic sulphite, &c., as under valeral, as an oily liquid of peculiar disagreeable smell, which boils at 152° and has sp. gr. ·827. As already mentioned (§ 172), this is probably *normal œnanthic aldehyde:*

$$CH_3.CH_2.CH_2.CH_2.CH_2.CH_2COH.$$

400*a*. The remaining known members of the series have been prepared by dry distillation of intimate mixtures of calcic formate with the calcic salts of the requisite acid, under reduced pressure (15–25 mm.) They are:—

Lauric aldehyde, $C_{11}H_{23}.CHO$, from lauric acid, melts at 44·5° and boils at 184°–185° under 100 mm. pressure. It forms a brilliant white, odourless, crystalline mass.

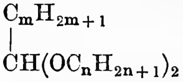
400*b*. *Myristic aldehyde,* $C_{13}H_{27}.CHO$, from myristic acid, melts at 52·5° and boils at 214°–215° under 100 mm. pressure.

401. *Palmitic aldehyde,* $C_{15}H_{31}.CHO$, from palmitic acid, forms nacreous leafy crystals, melting at 58·5°. Under 100 mm. pressure it boils at 239°–240°. By oxidation of cetylic alcohol a body is obtained melting at 52°, but it appears doubtful if this is palmitic aldehyde.

401*a*. *Stearic aldehyde,* $C_{17}H_{35}.CHO$, from stearic acid, crystallises in fine crystal leaves with bluish shimmer; it melts at 63·5° and boils at 259°–261° under 100 mm. pressure.

Ethereal Compounds of the Aldehyde Radicals.

402. The polymeric modifications of the aldehydes above mentioned may be classed amongst these compounds, as in them the several aldehyde radicals are held together by oxygen. In the true sense, however, the term is restricted to compounds in which aldehyde radicals and the monad alcohol radicals are joined together by oxygen, giving bodies of the general formula:



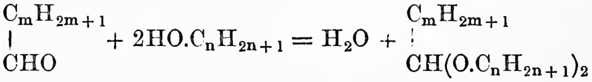
$$\begin{array}{l} C_mH_{2m+1} \\ | \\ CH(OC_nH_{2n+1})_2 \end{array}$$

The number of compounds known is not large, only those of methene and ethylidene having been prepared.

They were first obtained by incomplete oxidation of the respective primary alcohols, together with the aldehydes, one oxygen atom acting on three alcohol molecules according to the equation:

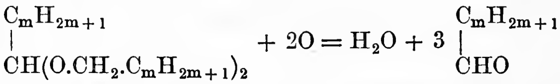
$$3C_nH_{2n+1}.OH + O = 2H_2O + C_nH_{2n}(OC_nH_{2n+1})_2.$$

These bodies are also obtained by mixing aldehydes with anhydrous alcohols, especially if the mixture be heated to 100° for some time:



$$\begin{array}{l} C_mH_{2m+1} \\ | \\ CHO \end{array} + 2HO.C_nH_{2n+1} = H_2O + \begin{array}{l} C_mH_{2m+1} \\ | \\ CH(O.C_nH_{2n+1})_2 \end{array}$$

By limited oxidation they are first converted into aldehydes:



$$\begin{array}{l} C_mH_{2m+1} \\ | \\ CH(O.CH_2.C_mH_{2m+1})_2 \end{array} + 2O = H_2O + 3 \begin{array}{l} C_mH_{2m+1} \\ | \\ CHO \end{array}$$

403. *Methene dimethylate, methylal,* or *formal,* $CH_3(O.CH_3)_2$, is obtained on heating methylic alcohol with manganic dioxide and sulphuric acid, and is separated from the crude distillate by fractional distillation. It is a colourless liquid which boils at 42° and has sp. gr. ·855. The vapour density is 2·625. With alcohol and ether formal can be mixed in every proportion; it dissolves in about three times its weight of water. On saturation of its aqueous solution with potassic hydrate it is again precipitated.

404. *Ethylidene dimethylate,* $CH_3.CH(O.CH_3)_2$, is found in crude wood spirit, and is prepared by oxidation of a mixture of methylic and ethylic alcohols, or more readily by heating aldehyde with absolute methylic alcohol. It is liquid, boils between 63° and 65°, and has sp. gr. ·8674 at 1° and a vapour density of 3·16.

Ethylidene methylate-ethylate, $CH_3.CH<\begin{array}{l}O.CH_3\\O.C_2H_5\end{array}$, is obtained, together with the foregoing, by oxidation of a mixture of ethylic and methylic alcohols, as a liquid boiling at 85°.

405. *Ethylidene ethylate*, *ethylidene diethyl-ether*, or *acetal*, $CH_3CH(O.C_2H_5)_2$, is formed by the oxidation of ethylic alcohol, and is contained in that fraction of the distillate coming over between 90° and 110°. By saturation of the liquid with calcic chloride it separates as an oil which floats on the surface, and is purified by fractional distillation. It is obtained more readily by heating aldehyde with absolute alcohol to 100°. Ethylidene dibromide, when treated with sodic ethylate, gives in part acetal:

$$CH_3.CHBr_2 + 2NaO.C_2H_5 = 2NaBr + CH_3CH.(O.C_2H_5)_2.$$

Ethylidene dichloride, on the other hand, yields monochlor-ethylene by similar treatment:

$$CH_3.CHCl_2 + NaO.C_2H_5 = NaCl + HO.C_2H_5 + CH_2:CHCl.$$

Acetal is a colourless, mobile liquid, of ·821 sp. gr. at 22·5°, which boils between 104° and 106°. It dissolves in eighteen volumes of water at 25°, but is less soluble at higher temperatures. On heating with acetic acid it gives aldehyde and ethylic acetate:

$$\begin{aligned}CH_3.CH(O.C_2H_5)_2 + 2HO.C_2H_3O = H_2O + CH_3.CHO\\ + 2C_2H_5.O.C_2H_3O.\end{aligned}$$

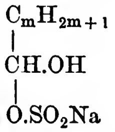
It is not attacked by potassic hydrate.

Sulphurous Acid Compounds of the Aldehydes.

406. As already mentioned (§ 389), the aldehydes unite with the hydric sulphites directly, and without formation of bye products, yielding crystalline compounds. By their properties these appear to be double sulphites containing the positive monad radical

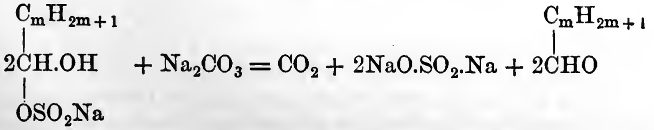
$$C_mH_{2m+1}.CH.OH.$$

Their constitution is therefore expressed by the general formula:



$$\begin{array}{l}C_mH_{2m+1}\\ |\\ CH.OH\\ |\\ O.SO_2Na\end{array}$$

They are readily decomposed by basic hydrates, or even by the carbonates of the alkalies, aldehyde being again formed:



$$\begin{array}{l}\;C_mH_{2m+1}\\ \;|\\ 2CH.OH\\ \;|\\ \;OSO_2Na\end{array} + Na_2CO_3 = CO_2 + 2NaO.SO_2.Na + \begin{array}{l}\;C_mH_{2m+1}\\ \;|\\ 2CHO\end{array}$$

The action of acids also causes the decomposition of these compounds into salts of the acids, aldehyde, and sulphurous acid.

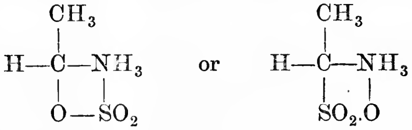
The hydric sulphite compounds of the lower members of the series are readily soluble in water, those of the higher members difficultly soluble; these latter, therefore, serve as a means of separating aldehydes from mixtures with other bodies. If the aldehydes in such mixtures be either difficultly soluble or insoluble in water, they must be shaken violently for a long time with saturated solution of the alkaline hydric sulphite, it being well to heat the mixture previously.

407. *Ethylidene-hydrate metallic sulphites,* or *aldehyde metallic sulphites,* $CH_3.CH(OH).O.SO_2M$. These compounds, which are readily soluble in water, are best prepared by slow addition of acetic aldehyde to well-cooled saturated solutions of the acid sulphites of the respective metals, until the liquid, after standing for some time in closed vessels, smells of aldehyde. From the solutions so prepared the crystalline salts are obtained either by precipitation with strong alcohol or by evaporation in a dry vacuum. On heating alone at 100° they decompose into aldehyde, sulphurous anhydride, and a neutral sulphite.

Ethylidene-hydrate potassic sulphite, $CH_3.CH(OH).O.SO_2K$, crystallises in tufts of needles the sodic salt $CH_3.CH(OH).O.SO_2Na$, by evaporation in fatty plates, by precipitation of its solution by alcohol in satiny needles. The ammonic salt prepared from aldehyde and hydric ammonic sulphite crystallises in small needles, which dissolve in six times their weight of water at 16° and in the dry state are not decomposed at 100°. It contains H_2O less than is required by the formula

$$C_2H_4(OH)O.SO_2NH_4,$$

and corresponds, very likely, to one of the formulæ



$$\begin{array}{c} CH_3 \\ | \\ H—C—NH_3 \\ |\qquad| \\ O—SO_2 \end{array} \qquad \text{or} \qquad \begin{array}{c} CH_3 \\ | \\ H—C—NH_3 \\ |\qquad| \\ SO_2.O \end{array}$$

probably by its stability at 100°, to the last. By dissolving baric carbonate in aqueous sulphurous acid mixed with excess of aldehyde and precipitating the filtered solution by alcohol, a satiny precipitate of the baric salt $(CH_3.CH(OH).O.SO_2)_2Ba$ is obtained.

408. In the case of the remaining aldehydes generally only the compounds with hydric sodic sulphite have been prepared. The propionic aldehyde compound is readily soluble; those of the higher molecular aldehydes separate on shaking with concentrated solution of hydric sodic sulphite, mostly in plates of silvery lustre, and the less soluble the richer in carbon the aldehyde is.

Oxychlorides of the Aldehyde Radicals.

409. In consequence of their divalent nature the aldehyde radicals can unite with two different elements, such as chlorine and oxygen, which latter, being diad, can still unite with other radicals. Chlorohydrates are not known, but chlor ethers and chlor salts exist.

410. *Dimethene chlor-oxide,* or *dichlor-methyl ether:*

$$C_2H_4Cl_2O = Cl.CH_2.O.CH_2.Cl,$$

is formed on carefully mixing dimethylic oxide and chlorine gases:

$$(CH_3)_2O + 2Cl_2 = (CH_2Cl)_2O + 2HCl,$$

and is separated from the liquid products by fractional distillation. It is a liquid boiling at 105°, of suffocating, tear-exciting odour, of sp. gr. 1·315 at 20°, decomposed by water into hydrochloric acid and formic aldehyde or paraformic aldehyde:

$$(CH_2Cl)_2O + H_2O = 2HCl + 2CH_2O.$$

411. *Ethylidene chloro-ethylate*, $CH_3.CHCl.O.C_2H_5$. If hydrochloric acid gas be conducted to saturation into a well-cooled mixture of aldehyde with twice its volume of absolute alcohol, the liquid separates into two layers, of which the upper contains ethylidene chlorethylate. By submitting this to fractional distillation it is obtained as an oil boiling at 97°–98°, which at every distillation is partially decomposed with evolution of hydrochloric acid.

With an alcoholic solution of sodic ethylate it yields acetal:

$$CH_3.CH{<}\begin{matrix}Cl\\O.C_2H_5\end{matrix} + NaO.C_2H_5 = NaCl + CH_3.CH{<}\begin{matrix}O.C_2H_5\\O.C_2H_5\end{matrix}$$

The same body is also obtained by the action of chlorine upon ethylic ether, whence its other name, *monochlor-ethylic ether* (§ 207).

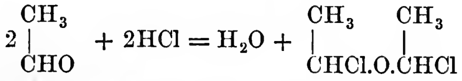
412. *Diethylidene chlor-oxide*, or *ethylidene oxychloride:*

$$CH_3.CHCl.O.CHCl.CH_3,$$

is formed by passing hydrochloric acid gas into aldehyde at 0°. The liquid divides into two layers, of which the upper is decanted, quickly dried by calcic chloride, and heated to 60°–70°, whilst a stream of carbonic anhydride is passed through it in order to remove any unaltered aldehyde. The residue is then fractioned, and the portion distilling between 116° and 117° collected. Pure ethylidene chloroxide is liquid, smells at once of aldehyde and hydrochloric acid, and has sp. gr. 1·1376 at 12°. It is not directly miscible with water, but is soon decomposed by it into hydrochloric acid and aldehyde:

$$(CH_3.CHCl)_2O + H_2O = 2HCl + 2CH_3.CHO.$$

Its formation is represented by the equation:



$$2\begin{matrix}CH_3\\|\\CHO\end{matrix} + 2HCl = H_2O + \begin{matrix}CH_3 & & CH_3\\| & & |\\CHCl & .O. & CHCl\end{matrix}$$

It is isomeric with bichlor ether (§ 207), which boils at 145°.

413. *Ethylidene chloro-acetate*, $CH_3.CH{<}\begin{matrix}Cl\\O.C_2H_3O\end{matrix}$. Aldehyde and acetic chloride unite directly with one another, when equal molecules are heated to 100° in sealed tubes:

$$CH_3.CHO + Cl.C_2H_3O = CH_3.CH{<}\begin{matrix}Cl\\O.C_2H_3O\end{matrix}$$

Ethylidene aceto-chloride is a liquid boiling at 120°–124°, which floats on water, and is slowly converted thereby into aldehyde, hydrochloric and acetic acids.

414. By passing hydrochloric acid gas into an alcoholic solution of œnanthic aldehyde, there is obtained amongst other products a *heptylidene chloro-ethylate:*

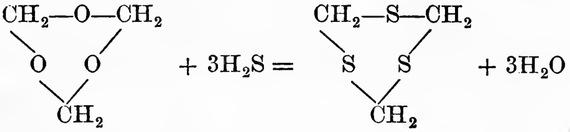
$$C_6H_{13}.CH<^{Cl}_{O.C_2H_5}$$

as a light oil which cannot be distilled unchanged.

Sulphur Compounds of the Alcohol Radicals.

415. On bringing an aldehyde and sulphuretted hydrogen together there result, frequently with formation of intermediate products, the thio-aldehydes, $C_mH_{2m+1}.CHS$, which as yet, however, are only known in polymeric modifications. These latter are crystalline bodies of unpleasant odour.

416. *Trimethene sulphide, parathioform-aldehyde,* $C_3H_6S_3$, is readily obtained by saturating paraform-aldehyde, or an aqueous solution of form-aldehyde, with hydric sulphide:



The same body is obtained by heating methene diiodide with an alcoholic solution of potassic sulphide:

$$3CH_2I_2 + 3K_2S = 6KI + C_3H_6S_3;$$

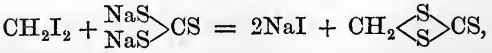
and by long standing of carbonic disulphide, granulated zinc, and dilute hydrochloric acid:

$$3CS_2 + 6Zn + 12HCl = C_3H_6S_3 + 3H_2S + 6ZnCl_2.$$

Trimethene sulphide is nearly insoluble in water, difficultly soluble in alcohol and ether, more readily in carbonic disulphide, and most soluble in benzene. It crystallises in interlaced needles of extremely disagreeable, onion-like odour, which begin to sublime at 150°, but melt at 218°. The found vapour density is 4·98, that required for the formula $C_3H_6S_3$ being 4·77.

With an alcoholic solution of mercuric chloride it yields silky needles, quite insoluble in water, of the formula $C_3H_6S_3HgCl_2$; with argentic nitrate, plates, which can be recrystallised from hot water, of $C_3H_6S_3AgNO_3,H_2O$, and gives with platinic chloride $(C_3H_6S_3)_2PtCl_4$. By heating at 170° with argentic sulphate it yields paraform-aldehyde, $C_3H_6O_3$.

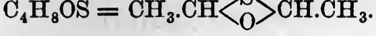
Methene sulpho-carbonate is obtained by heating methene diiodides with an alcoholic solution of sodic sulpho-carbonate:



$$CH_2I_2 + {}^{NaS}_{NaS}>CS = 2NaI + CH_2<^{S}_{S}>CS,$$

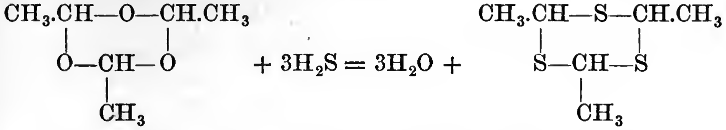
as a yellowish white amorphous powder. The molecular formula is probably a multiple of the above given.

417. *Thioacetic Aldehyde, or Ethylidene Sulphide.*—By passing hydric sulphide into aldehyde there is first formed an oily body of nauseous odour, containing equal molecules of aldehyde and thioaldehyde:



$$C_4H_8OS = CH_3.CH{<}\substack{S\\O}{>}CH.CH_3.$$

This solidifies when strongly cooled, melts again at −2°, and at 35° begins to boil with decomposition, pure aldehyde passing over. By treatment with acids it is split up into aldehyde and solid parathioaldehyde, or triethylidene trisulphide, $C_6H_{12}S_3$. In consequence of this only the latter body is obtained when sulphuretted hydrogen is conducted into strongly acidulated aldehyde. It is also readily prepared from paraldehyde:



Thio-paraldehyde crystallises in colourless needles of garlic odour, insoluble in water, but soluble in alcohol and ether, and slowly subliming on gentle heating. The vapour density is found to be 6·199, corresponding to the molecular formula $C_6H_{12}S_3$, which requires 6·22.

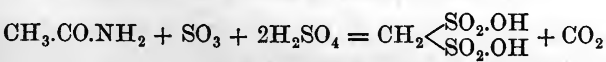
418. The thio-aldehydes richer in carbon are less known. Isobutyric aldehyde is converted by sulphuretted hydrogen into an oil of unpleasant, onion-like odour, and which has not yet been obtained in the crystalline state.

Isovaleric aldehyde only reacts with sulphuretted hydrogen when in aqueous solution. There results a crystalline mass of *isoamylidene sulphide*, $\substack{CH_3\\CH_3}{>}CH.CH_2.CHS$. Re-crystallised from alcohol or ether, this isovaleric thio-aldehyde forms white, asbestos-like crystals of nauseous odour, which melt at 69° and can only be volatilised unchanged in vacuo. The vapour density = found 3·508, calculated 3·525.

A *selenio-isovaleric aldehyde* is obtained from valeral and hydric selenide in crystalline crusts of fearful odour. It melts at 56·5°, sublimes even at ordinary temperatures, and is readily decomposed with separation of selenium.

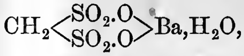
Sulphonic Acids of the Aldehyde Radicals.

419. Methene forms a *methen-disulphonic acid,* generally termed *methionic acid,* $CH_2(SO_2.OH)_2$, which can be obtained by oxidation of methene sulpho-carbonate by nitric acid. It is also formed in small quantity by the action of sulphuric anhydride upon ethylic ether, more readily by heating acetamide or acetonitrile with Nordhausen sulphuric acid, the reaction being probably as follows:



$$CH_3.CO.NH_2 + SO_3 + 2H_2SO_4 = CH_2{<}\substack{SO_2.OH\\SO_2.OH} + CO_2 + NH_4.H.SO_4.$$

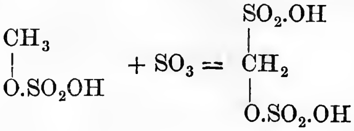
The free acid crystallises in long, deliquescent needles, and is not altered by boiling nitric acid. On mixing its solution with baric chloride, baric methen-disulphonate:



$$CH_2{<}\begin{matrix}SO_2.O\\SO_2.O\end{matrix}{>}Ba,H_2O,$$

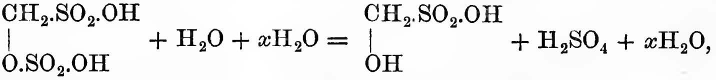
separates in difficultly soluble, nacreous scales, which can be recrystallised from boiling hydrochloric acid.

420. *Methene-hydrate sulphonic acid*, $CH_2(OH).SO_2.OH$, is formed when the vapour of sulphuric anhydride is passed into a well-cooled mixture of methylic alcohol and sulphuric acid. As this mixture would contain hydric methylic sulphate, the process probably is as follows:



$$\begin{array}{l}CH_3\\ |\\ O.SO_2OH\end{array} + SO_3 = \begin{array}{l}SO_2.OH\\ |\\ CH_2\\ |\\ O.SO_2.OH\end{array}$$

The liquid is then boiled with water for several hours:



$$\begin{array}{l}CH_2.SO_2.OH\\ |\\ O.SO_2.OH\end{array} + H_2O + xH_2O = \begin{array}{l}CH_2.SO_2.OH\\ |\\ OH\end{array} + H_2SO_4 + xH_2O,$$

and neutralised with plumbic carbonate whilst still boiling.

The liquid, filtered from the plumbic sulphate, contains plumbic methene-hydrate sulphonate; this is decomposed by hydric sulphide, and after filtration of the precipitated plumbic sulphide is saturated with metallic carbonates in order to prepare the respective salts. The potassic salt, $CH_2.(OH).SO_2OK$, crystallises in the rhombic system the baric salt in colourless tables. Both free acid and salts are very stable.

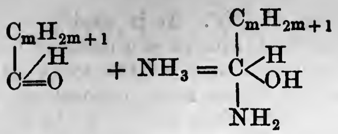
421. Ethylidene disulphonic acid is not known, but on heating ethylidene dichloride with normal sodic sulphite at 140° in sealed tubes a salt of *ethylidene chlor-sulphonic acid* is obtained:

$$CH_3.CH\left\{\begin{matrix}Cl\\Cl\end{matrix}\right. + NaSO_2.ONa = NaCl + CH_3.CH\left\{\begin{matrix}Cl\\SO_2.ONa\end{matrix}\right.$$

To purify the compound the contents of the tube are treated with excess of sulphuric acid and evaporated, in order to decompose sodic chloride and excess of sodic sulphite. The residual acid mass is then neutralised with sodic hydrate, evaporated to complete dryness, treated with boiling absolute alcohol, and filtered. This dissolves the ethylidene chloro-sulphonate, and on cooling the filtrate, nacreous plates of the above-given formula separate. The baric salt crystallises in warty masses. Both salts, as also the acid, are very stable bodies.

Nitrogen Compounds of the Alcohol Radicals.

422. Most aldehydes unite directly—with evolution of heat—with one molecule of ammonia, yielding crystalline compounds, the *aldehyde ammonias*, which behave as the *hydrate amides* of the diad radicals:



$$\begin{array}{l}C_mH_{2m+1}\\ |\;\diagup H\\ C{=}O\end{array} + NH_3 = \begin{array}{l}C_mH_{2m+1}\\ |\\ C\begin{smallmatrix}H\\OH\end{smallmatrix}\\ |\\ NH_2\end{array}$$

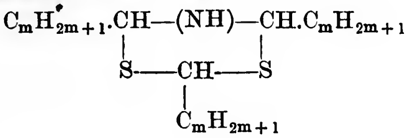
These compounds readily yield aldehyde when treated with acids :

$$C_mH_{2m+1}.CH(OH)NH_2 + H_2SO_4 = C_mH_{2m+1}.CHO + NH_4.HSO_4.$$

By passing hydric sulphide into the aqueous solution of these substances water and ammonic sulphide are formed, and crystals of sulphuretted bases, the *thialdines*, separate :

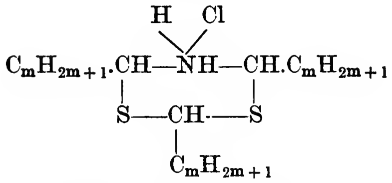
$$3(C_mH_{2m+1}.CH.OH.NH_2) + 3H_2S = 3H_2O + (NH_4)_2S$$
$$+ (C_mH_{2m+1}.CH)_3NH.S_2,$$

which yield crystalline salts with one equivalent of acid. These thialdines and their salts are probably bodies of the constitution expressed by the general formulæ:



$$\begin{array}{c}C_mH_{2m+1}.CH{-}(NH){-}CH.C_mH_{2m+1}\\ \;|\qquad\qquad\quad |\\ S{-\!-}CH{-\!-}S\\ |\\ C_mH_{2m+1}\end{array}$$

and



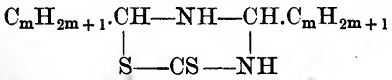
$$\begin{array}{c}H\quad Cl\\ \diagdown\diagup\\ C_mH_{2m+1}.CH{-}NH{-}CH.C_mH_{2m+1}\\ |\qquad\qquad |\\ S{-\!-}CH{-\!-}S\\ |\\ C_mH_{2m+1}\end{array}$$

i.e. imide disulphides of three aldehyde radicals.

If an alcoholic solution of an aldehyde ammonia be treated with carbonic disulphide, crystalline bodies, termed *carbo-thialdines*, are obtained:

$$2C_nH_{2n}.OH.NH_2 + CS_2 = 2H_2O + (C_nH_{2n})_2N_2H_2CS_2,$$

whose constitution is probably expressed by the formula :



$$\begin{array}{c}C_mH_{2m+1}.CH{-}NH{-}CH.C_mH_{2m+1}\\ |\qquad\qquad |\\ S{-\!-}CS{-\!-}NH\end{array}$$

In addition to the hydrate amides, aldehydes also yield with ammonia other products, which contain no oxygen; these have the character of nitrile bases of the aldehyde radicals.

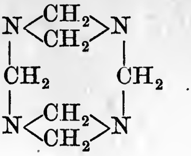
423. On adding methene oxide, best in the form of paraformic aldehyde, to ammonia, there is obtained *hexmethene tetramine*, also termed *hexmethylenamine*, according to the equation :

$$2C_3H_6O_3 + 4NH_3 = 6H_2O + C_6H_{12}N_4.$$

It crystallises from alcohol in brilliant colourless prisms or rhombohedrons, which have an unpleasant odour on heating, and partly sublime undecomposed at 100°. It is readily soluble in water, difficultly in cold alcohol, and behaves as a monacid base.

With hydrochloric acid it gives the salt $C_6H_{12}N_4.HCl$, crystallising in white needles, whose aqueous solution yields with platinic chloride a precipitate of the formula $2C_6H_{12}N_4HCl,PtCl_4$.

The structural formula of hexamethene tetramine is probably

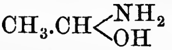


By boiling with dilute acids it is reconverted into formic aldehyde:

$$(CH_2)_6N_4,HCl + 3HCl + 6H_2O = 4NH_4Cl + 6CH_2O.$$

Methene hydrate-amide is not known.

424. *Ethylidene hydrate-amide*, or *aldehyde ammonia*:

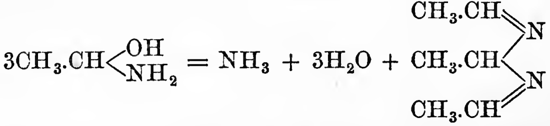


$$CH_3.CH\left\langle\begin{matrix}NH_2\\OH\end{matrix}\right.$$

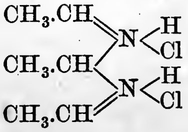
separates in well-formed colourless rhombohedra when dry ammonia is passed into a mixture of anhydrous ether and acetic aldehyde. The crystals have a peculiar odour, like that of the excrements of mice, and are very soluble in water, as also in alcohol. The vapour density determined at 100°–160° in vacuo is 2·098 the number calculated from the molecular formula being 2·108. At reduced pressures aldehyde ammonia can be obtained at these temperatures in the state of vapour, but at ordinary atmospheric pressure it decomposes below 100°, and still more quickly if water be present, turning yellow or brown, and yielding water, ammonia, and amorphous basic oxytetraldine:

$$4CH_3.CH(OH).NH_2 = 3NH_3 + 3H_2O + \underset{\text{(Oxytetraldine.)}}{C_8H_{13}NO}.$$

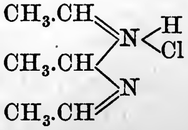
It suffers a similar decomposition when left for a long time either when damp or in presence of alcohol, being thereby converted into an amorphous oxygen free base—*hydracetamide* or *aldehydine*, $C_6H_{12}N_2$, which probably is triethylidene diamine:



This body is insoluble in ether, but readily soluble in alcohol and water, and yields with acids amorphous soluble salts, which may contain either one or two equivalents of acid; e.g.



and



Both these compounds give precipitates with platinic chloride, of which $C_6H_{12}N_2,2HCl,PtCl_4$ is a sandy, crystalline body, whilst $(C_6H_{12}N_2,HCl)_2,PtCl_4$ is amorphous.

If the diacid salt be boiled with water it gives ammonic chloride and *oxy-trialdine hydrochloride :*

$$(CH_3.CH:)_3N_2,2HCl + H_2O = NH_4Cl + C_6H_{11}NO,HCl.$$

Oxy-trialdine is also obtained on evaporating a solution of aldehydine at the temperature of the water bath :

$$(CH_3.CH:)_3N_2 + H_2O = NH_3 + C_6H_{11}NO,$$

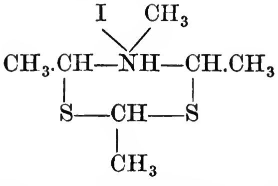
as a brown, amorphous, weakly basic subtance. In this, as in oxy-tetraldine, the ethylidene group no longer occurs, but a complicated carbon nucleus formed by simultaneous union of such groups (compare pyridene bases).

425. If an aqueous solution of aldehyde ammonia be saturated with sulphurous anhydride and then evaporated, a crystalline body remains, of the formula $C_2H_7NSO_3$, which is not identical with that prepared from hydric ammonic sulphite and aldehyde (§ 407), but only isomeric therewith. It dissolves in one and a half times its weight of water, and decomposes at 100° with formation of a resinous brown mass.

426. By passing sulphuretted hydrogen gas into an aqueous solution of aldehyde ammonia, brilliant colourless crystals of *thialdine*, $C_6H_{13}NS_2 = (CH_3.CH)_3S_2.NH$, separate. These are little soluble in water, but readily in alcohol and ether, fuse at 42°, and can be sublimed. Its nauseous odour is very persistent. Thialdine gives salts with hydrochloric and nitric acids :

$$C_6H_{13}NS_2,HCl \text{ and } C_6H_{13}NS_2,HNO_3.$$

Heated with argentic nitrate, it decomposes into aldehyde, ammonic nitrate, and argentic sulphide. Alcoholic iodides unite directly with it. Methylic iodide, for instance, yields, after some hours at ordinary temperatures, *methyl-thialdine iodide :*



Aldehyde ammonia unites with hydric selenide to form selenaldine, $C_6H_{13}NSe_2 = (CH_3.CH:)_3Se_2NH$.

427. *Carbo-thialdine*, $C_5H_{10}N_2S_2$, separates on mixing an alcoholic solution of aldehyde ammonia with carbonic disulphide in brilliant colourless crystals, which only dissolve readily in hot alcohol, not in water or ether, and on boiling with acids decompose again into aldehyde, carbonic disulphide, and ammonic salts.

428. *Butyricaldehyde-ammonia*, $CH_3.CH_2.CH_2.CH(OH)NH_2$, and *isobutyric aldehyde-ammonia*, $(CH_3)_2:CH.CH(OH).NH_2$, are also known. From the latter there have been prepared *thio-isobutaldine*, $[(CH_3)_2:CH.CH]_3S_2NH$, as a difficultly crystallisable mass, and *carbo-isobutaldine*, $[(CH_3)_2:CH.CH_2]_2CS_2(NH_2)$, in colourless prisms, melting at 91°.

429. *Isovaleric aldehyde-ammonia, isoamylidene hydrate-amide,* or *valeral ammonia,* $(CH_3)_2:CH.CH_2.CH(OH)NH_2,7H_2O$, is nearly insoluble in water, but considerably soluble in alcohol and ether, even when they contain water. On heating, the crystals fuse and lose their water of crystallisation, becoming again crystalline on cooling. The vapour density in vacuo at 160° = 3·6, calculated 3·559. On adding strong aqueous ammonia to a mixture of valeral and carbonic disulphide, *carbo-thio-valeraldine,* $C_{11}H_{22}N_2S_2$, or

$$[(CH_3)_2:CH.CH_2.CH]_2.CS_2.(NH_2)_2$$

separates in warty crystals, which melt at 115·5°–117°.

Thio-valeraldine, $C_{15}H_{31}NS_2$, or $[(CH_3)_2:CH.CH_2.CH_2]_3S_2NH$, is obtained as an oily body on passing dry ammonia gas over thio-isovaleric aldehyde:

$$3C_5H_{10}S + 2NH_3 = C_{15}H_{31}NS_2 + NH_4.SH.$$

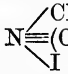
On heating valeral ammonia with potassic hydrate, three molecules of the compound lose two molecules of ammonia, and a basic body is formed, which can be distilled with aqueous vapour, and has the formula $C_{15}H_{33}NO_3$, and therefore contains the elements of three molecules of valeral and of one molecule of ammonia. It is probably the nitrile base of isoamylidene hydrate:

$$3(CH_3)_2:CH.CH_2.CH(OH).NH_2 = 2NH_3 + [(CH_3):CH.CH_2.CH(OH)]_3N.$$

Œnanthol also yields an ammonia compound, $C_6H_{13}.CH(OH).NH_2$.

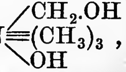
430. By gentle heating of methene diiodide with alcoholic trimethylamine solution, there is formed, according to the equation:

$$CH_2I_2 + N(CH_3)_3 = N(CH_2I)(CH_3)_3I,$$

Iodo-methene trimethyl ammonic iodide,  $N\begin{cases}CH_2.I\\(CH_3)_3\\I\end{cases}$, crystallising in needles, and readily yielding with moist argentic oxide the basic

Iodo-methene trimethyl ammonic hydrate:

$$N(CH_2I)(CH_3)_3.OH.$$

If the aqueous solution be boiled for a long time with excess of argentic hydrate, argentic iodide again separates, and the strongly alkaline *methene-hydrate trimethyl ammonic hydrate,*  $N\begin{cases}CH_2.OH\\(CH_3)_3\\OH\end{cases}$, is now contained in solution. Both bases yield salts with acids. The chlorides combine with platinic chloride and form

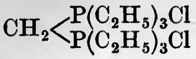
$[N(CH_2I)(CH_3)_3Cl]_2,PtCl_4$, crystallising in tables:
$[N(CH_2.OH)(CH_3)_3Cl]_2PtCl_4$, in octahedra.

431. Methene diiodide unites with triethyl phosphine, forming

Iodo-methene triethyl phosphonic iodide, $P(CH_2I)(C_2H_5)_3I$, from which—corresponding to the above ammonic hydrate compounds—the phosphonic hydrates $P(CH_2I)(C_2H_5)_3OH$ and

$$P(CH_2.OH)(C_2H_5)_3.OH$$

can be obtained. Methene dichloride yields with triethyl phosphine chlor-methene, triethyl phosphonic chloride, $P(CH_2Cl)(C_2H_5)_3Cl$, together with methene hexethyl diphosphonic dichloride:



$$CH_2\!<\!\begin{matrix}P(C_2H_5)_3Cl\\ P(C_2H_5)_3Cl\end{matrix}$$

432. The metallic and halogen substitution derivatives of the nitro-paraffins, already mentioned (§§ 289–292), must be regarded as derivatives of the aldehyde radicals.

Nitro-sodium methene = $CH_2.Na.(NO_2)$ = sodium nitro-methene (§ 296).

Nitro-mercury dimethene = $NO_2.CH_2.Hg.CH_2.NO_2$.

Nitro-sodium ethylidene = $CH_3.CH.Na(NO_2)$ = sodium nitro-ethane.

Ethylidene nitro-bromide = $CH_3.CHBr(NO_2)$ = brom-nitro-ethane, boiling at 145°–148° (both § 291), &c.

432*a*. *Dinitro-ethane*, $CH_3.CH(NO_2)_2$, prepared by treatment of brom-nitro-ethane with alcoholic potash and potassic nitrite and decomposition of the resulting potassium derivative with an acid, is a colourless refractive liquid, boils at 185°–186°, and has sp. gr. 1·3503 at 23·5°.

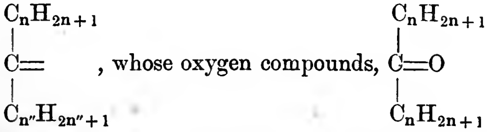
α-Dinitro-propane, $CH_3.CH_2.CH(NO_2)_2$, prepared in similar manner from α-brom-nitro-propane, is a colourless oil, boils at 189°, and has sp. gr. ·8335 at 0°.

β-Dinitro-propane, $CH_3.C(NO_2)_2.CH_3$, is a white, crystalline, camphor-like solid, melting at 53° and boiling at 185·5°. It is prepared by oxidising the body $C_3H_6N_2O_3$, obtained by the action of sulphuric acid on a mixture of potassic nitrite and β-nitro-propane dissolved in potassic hydrate.

KETONE DERIVATIVES.

Compounds of the Radicals $\left.\begin{matrix}C_{n'}H_{2n'+1}\\ C_{n''}H_{2n''+1}\end{matrix}\right\}C{=}$

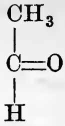
433. By replacement of two hydrogen atoms of a paraffin on one and the same intermediate carbon atom, there result derivatives of the diad radicals:



$$\begin{array}{c}C_nH_{2n+1}\\ |\\ C{=}\\ |\\ C_{n''}H_{2n''+1}\end{array}\text{, whose oxygen compounds, }\begin{array}{c}C_nH_{2n+1}\\ |\\ C{=}O\\ |\\ C_nH_{2n+1}\end{array}$$

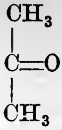
are termed ketones or acetones. It is self-evident that the paraffin poorest in carbon that can yield a ketone is propane, and the lowest member of the homologous ketone series $C_nH_{2n}O$ is acetone, C_3H_6O or $CH_3.CO.CH_3$, isomeric with propionic aldehyde. This first member has been (as regards its chemical reactions) by far the best investigated. A large number of higher homologues are known, but their derivatives have mostly not been prepared.

Considering the alcohol radicals as compounds of carboxyl, CO, with a hydrogen atom and an alcohol radical, the ketones would appear as compounds of carboxyl with two alcohol radicals, or as aldehydes in which the hydrogen atom in union with CO has been replaced by an alcohol radical:



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

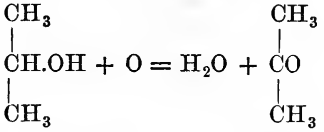
Acetic aldehyde.



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

Acetone.

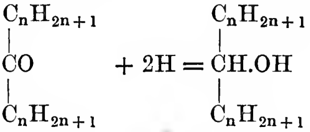
434. The ketones are the first oxidation products of the secondary alcohols (§ 160, 2), as the isomeric aldehydes are of the primary alcohols:



$$\begin{array}{c} CH_3 \\ | \\ CH.OH \\ | \\ CH_3 \end{array} + O = H_2O + \begin{array}{c} CH_3 \\ | \\ CO \\ | \\ CH_3 \end{array}$$

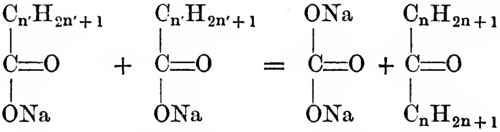
Secondary propylic alcohol. Acetone.

and similarly, by treatment with nascent hydrogen (when their aqueous or aqueo-alcoholic solutions are treated with sodium amalgam), are converted into secondary alcohols:



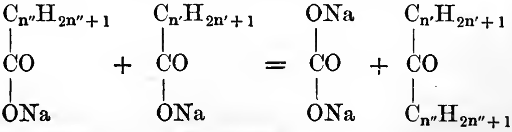
$$\begin{array}{c} C_nH_{2n+1} \\ | \\ CO \\ | \\ C_nH_{2n+1} \end{array} + 2H = \begin{array}{c} C_nH_{2n+1} \\ | \\ CH.OH \\ | \\ C_nH_{2n+1} \end{array}$$

435. A method of general application for the synthetical preparation of ketones consists in the dry distillation of the salts of monobasic organic acids of the formula $C_nH_{2n-1}O.OH$. If such salts be submitted to high temperatures in absence of air, a metallic carbonate is left, whilst a ketone is evolved as the main product. From a salt of a single organic acid a ketone is obtained whose two alcohol radicals are similar:



$$\begin{array}{c} C_{n'}H_{2n'+1} \\ | \\ C{=}O \\ | \\ ONa \end{array} + \begin{array}{c} C_{n'}H_{2n'+1} \\ | \\ C{=}O \\ | \\ ONa \end{array} = \begin{array}{c} ONa \\ | \\ C{=}O \\ | \\ ONa \end{array} + \begin{array}{c} C_nH_{2n+1} \\ | \\ C{=}O \\ | \\ C_nH_{2n+1} \end{array}$$

A mixture of the salts of two acids, on the other hand, yields, in addition to the two respective ketones containing similar alcohol radicals, also one containing two dissimilar alcohol radicals:



$$\begin{array}{c} C_{n''}H_{2n''+1} \\ | \\ CO \\ | \\ ONa \end{array} + \begin{array}{c} C_{n'}H_{2n'+1} \\ | \\ CO \\ | \\ ONa \end{array} = \begin{array}{c} ONa \\ | \\ CO \\ | \\ ONa \end{array} + \begin{array}{c} C_{n'}H_{2n'+1} \\ | \\ CO \\ | \\ C_{n''}H_{2n''+1} \end{array}$$

It is evident that these reactions correspond to the formation of aldehydes by the dry distillation of salts of higher molecular organic acids with formates, as

$$H.CO.ONa + CH_3.CO.ONa = CO(ONa)_2 + H.CO.CH_3;$$

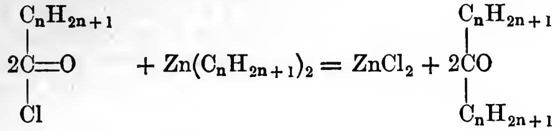
so similarly:

$$CH_3.CO.ONa + CH_3.CO.ONa = CO(ONa)_2 + CH_3.CO.CH_3.$$

The ketone obtained as main product contains invariably a carbon atom less than the sum of those contained in the two salt molecules from which it is derived.

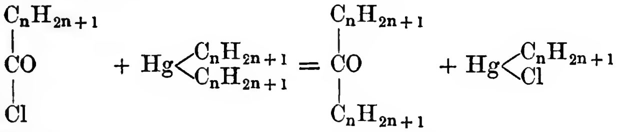
436. The following are of especial importance amongst the further methods for the synthetical preparation of ketones:—

1. By the action of the acid chlorides, $C_nH_{2n+1}.CO.Cl$, upon a molecule of a zinc dialkyl, a ketone is formed together with zincic chloride:



$$2\begin{array}{c}C_nH_{2n+1}\\|\\C{=}O\\|\\Cl\end{array} + Zn(C_nH_{2n+1})_2 = ZnCl_2 + 2\begin{array}{c}C_nH_{2n+1}\\|\\CO\\|\\C_nH_{2n+1}\end{array}$$

In place of the zinc alkyl, the mercury compound of an alcohol radical can be employed, whereby, however, only one molecule of the acid chloride reacts:



$$\begin{array}{c}C_nH_{2n+1}\\|\\CO\\|\\Cl\end{array} + Hg{<}\begin{array}{l}C_nH_{2n+1}\\C_nH_{2n+1}\end{array} = \begin{array}{c}C_nH_{2n+1}\\|\\CO\\|\\C_nH_{2n+1}\end{array} + Hg{<}\begin{array}{l}C_nH_{2n+1}\\Cl\end{array}$$

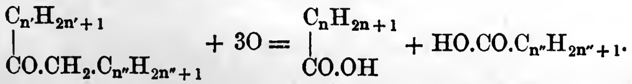
2. Another way, which, however, only serves for such ketones as contain methyl as one of the alcohol radicals ($CH_3.CO.C_nH_{2n+1}$), is from ethylic aceto-sod-acetate, $CH_3.CO.CHNa.CO.C_2H_5$. This latter is first heated with an alkylic haloid:

$$CH_3.CO.CHNa.CO.O.C_2H_5 + IC_nH_{2n+1} = NaI$$
$$+ CH_3.CO.CH(C_nH_{2n+1})CO.O.C_2H_5,$$

and the resulting ethylic alkyl aceto-acetate decomposed by boiling with alkalies or baric hydrate:

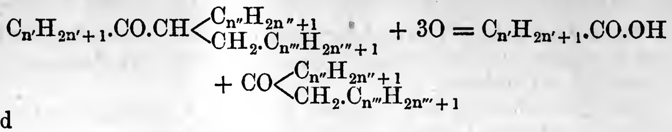
$$CH_3.CO.CH(C_nH_{2n+1}).CO.O.C_2H_5 + 2KOH = CO(OK)_2$$
$$+ C_2H_5.OH + CH_3.CO.CH_2(C_nH_{2n+1}).$$

437. In comparison with the aldehydes the ketones are only difficultly attacked by oxidising agents. By energetic action, as by boiling with chromic and sulphuric acids, or by fusion with alkaline hydrates, every ketone is converted into at least two acid molecules, of which one contains the CO group with one alcohol radical, whilst the other is formed from the second alcohol group, provided it be primary:



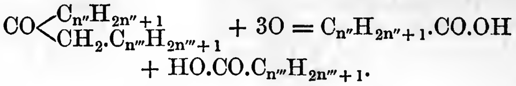
$$\begin{array}{l}C_{n'}H_{2n'+1}\\|\\CO.CH_2.C_{n''}H_{2n''+1}\end{array} + 3O = \begin{array}{l}C_nH_{2n+1}\\|\\CO.OH\end{array} + HO.CO.C_{n''}H_{2n''+1}.$$

Acetic acid always results from ketones containing the methyl group. If, on the other hand, the alkyl separated from CO be secondary, there occurs, together with the acid in the first line, a new ketone, which is further oxidised to two acid molecules:



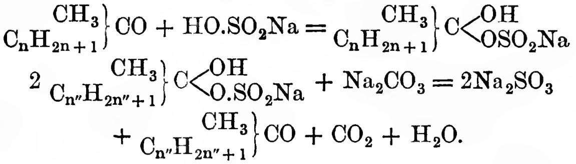
$$C_{n'}H_{2n'+1}.CO.CH\Big<\begin{array}{l}C_{n''}H_{2n''+1}\\CH_2.C_{n'''}H_{2n'''+1}\end{array} + 3O = C_{n'}H_{2n'+1}.CO.OH + CO\Big<\begin{array}{l}C_{n''}H_{2n''+1}\\CH_2.C_{n'''}H_{2n'''+1}\end{array}$$

and



$$CO\Big<\begin{array}{l}C_{n''}H_{2n''+1}\\CH_2.C_{n'''}H_{2n'''+1}\end{array} + 3O = C_{n''}H_{2n''+1}.CO.OH + HO.CO.C_{n'''}H_{2n'''+1}.$$

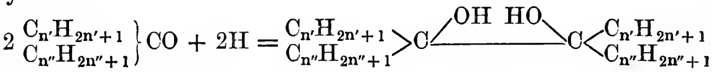
438. In analogy to the aldehydes (§ 406) many of the ketones unite with the alkaline hydric sulphites to form compounds which crystallise in silky plates, and from which the ketone is regenerated on treatment with alkaline carbonates. These compounds appear to be restricted to the ketones containing methyl:



$$\left.\begin{array}{r}CH_3\\C_nH_{2n+1}\end{array}\right\}CO + HO.SO_2Na = \left.\begin{array}{r}CH_3\\C_nH_{2n+1}\end{array}\right\}C\Big<\begin{array}{l}OH\\OSO_2Na\end{array}$$

$$2\left.\begin{array}{r}CH_3\\C_{n''}H_{2n''+1}\end{array}\right\}C\Big<\begin{array}{l}OH\\O.SO_2Na\end{array} + Na_2CO_3 = 2Na_2SO_3 + \left.\begin{array}{r}CH_3\\C_{n''}H_{2n''+1}\end{array}\right\}CO + CO_2 + H_2O.$$

439. By moderated action of nascent hydrogen, the ketones yield, together with the secondary alcohols, double tertiary diacid alcohols, termed *pinacones* (§ 456), which are formed by true carbon nucleus synthesis:

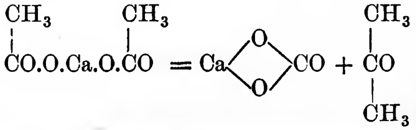


$$2\left.\begin{array}{l}C_{n'}H_{2n'+1}\\C_{n''}H_{2n''+1}\end{array}\right\}CO + 2H = \begin{array}{l}C_{n'}H_{2n'+1}\\C_{n''}H_{2n''+1}\end{array}\!\!>C\overset{OH\quad\quad HO}{\text{———————}}C\Big<\begin{array}{l}C_{n'}H_{2n'+1}\\C_{n''}H_{2n''+1}\end{array}$$

Dehydrating agents, such as concentrated sulphuric acid, &c., when heated with ketones, also cause synthesis of more complex molecules (so termed condensation), but of different nature. These and other changes will be considered under acetone.

Acetone, $C_3H_6O = CH_3.CO.CH_3$.

440. *Acetone*, or *dimethyl ketone*, isomeric with propionic aldehyde (§ 396), is most readily obtained by dry distillation of acetates, especially the calcic salt:



It is also obtained from acetic acid by conducting its vapour through tubes heated to dull redness:

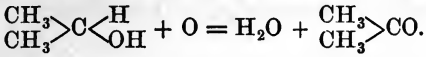
$$2CH_3.CO.OH = CO + H_2O + CH_3.CO.CH_3.$$

It is further formed by the dry distillation of sugars, cellulose, tartaric acid, citric acid, and other organic bodies, and is therefore a constituent of crude wood spirit (§ 165).

If acetic chloride diluted with anhydrous ether be slowly mixed with zinc methyl, the two ingredients react, forming zincic chloride and acetone:

$$2CH_3.COCl + Zn(CH_3)_2 + ZnCl_2 + 2CH_3.CO.CH_3.$$

Isopropylic alcohol is very readily converted into acetone by oxidising agents:



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!C\!<\!\begin{matrix}H\\OH\end{matrix} + O = H_2O + \begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CO.$$

Other methods of formation of acetone will be mentioned later, such as from propylene and glyceryl derivatives, from ethylic methyl-aceto-acetate, &c.

441. For the preparation of acetone, calcic acetate is usually heated to dull redness in an iron retort. The crude distillate is then dried by calcic chloride and submitted to fractional distillation. The portion distilling at 56° is nearly pure acetone.

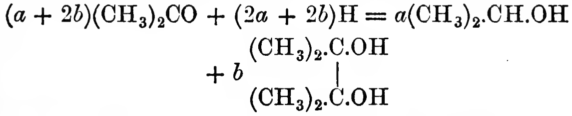
Crude acetone is also obtained in large quantity as a bye product in the preparation of aniline (which see).

If acetone be required in a state of perfect purity, purified acetone must be shaken with a concentrated solution of hydric sodic sulphite, so as to convert it into its crystalline compound with this latter. This is then pressed, washed with alcohol and ether, completely dried, and decomposed by boiling solution of sodic hydrate in a distillation apparatus. The aqueous acetone which goes over is then dried with calcic chloride and finally rectified.

442. Acetone is a colourless, mobile liquid of peculiar agreeable odour, of sp. gr. ·814 at 0° and boiling at 86°. Its vapour burns readily in air with a luminous but not smoky flame. It mixes in all proportions with alcohol, ether, and water. From the latter it is in great part separated on addition of very soluble salts, such as calcic chloride.

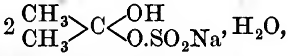
Like alcohol, it dissolves many substances insoluble in water (fats, colouring matters, &c.)

When acetone is treated in aqueous solution with sodium amalgam, it yields isopropylic alcohol (§ 168, 2) together with pinacone:



$$(a + 2b)(CH_3)_2CO + (2a + 2b)H = a(CH_3)_2.CH.OH + b\begin{matrix}(CH_3)_2.C.OH\\|\\(CH_3)_2.C.OH\end{matrix}$$

The compound of acetone with hydric sodic sulphite:



$$2\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!C\!<\!\begin{matrix}OH\\O.SO_2Na\end{matrix}, H_2O,$$

which crystallises in nacreous prisms, is pretty soluble in pure water, more difficultly so when the liquid contains much hydric salt or acetone. It is also in great part precipitated by alcohol. The similar potassic compound is anhydrous.

443. Acetone is oxidised to acetic and formic acids by a solution of potassic bichromate and sulphuric acid, especially on gentle heating:

$$CH_3.CO.CH_3 + K_2Cr_2O_7 + 4H_2SO_4 = K_2Cr_2(SO_4)_4 + 4H_2O + CH_3.CO.OH + HCO.OH,$$

the formic acid being in great part further oxidised to carbonic anhydride and water.

An analogous reaction occurs on passing acetone over heated alkalies, best potash lime or soda lime:

$$CH_3.CO.CH_3 + 2KOH + H_2O = CH_3.CO.OK + HCO.OK + 3H_2.$$

At the same time, especially at higher temperatures, another process occurs, which yields carbonates and methane:

$$(CH_3)_2CO + 2HOK = CO(OK)_2 + 2CH_4.$$

444. Strong mineral acids, such as sulphuric acid, and further alkalies and quick-lime, on gentle heating withdraw water from several molecules of acetone, and yield, by coalescence of the residues, compounds richer in carbon. The chief products of these reactions are *mesityl oxide*, $C_6H_{10}O$, *phorone*, $C_9H_{14}O$, and *mesitylene*, C_9H_{12}, a liquid hydro-carbon, boiling at 163°, which is described later.

Mesityl oxide is formed according to the equation:

$$2(CH_3)_2CO = H_2O + C_6H_{10}O.$$

It is a mobile, colourless liquid, of peppermint odour, which boils at 130°, and itself possesses the properties of a ketone inasmuch as it takes up nascent hydrogen, and with phosphoric chloride gives phosphoric oxychloride and a chloride of the formula $C_6H_{10}Cl_2$.

Phorone, formed according to the equation:

$$3C_3H_6O = 2H_2O + C_9H_{14}O,$$

crystallises in large brittle prisms, melting at 28° and boiling at 196°.

Mesityl oxide and phorone are best prepared by saturating acetone with hydrochloric acid gas. The product is allowed to stand about a fortnight in closed vessels, and then on addition of water gives a yellow chlorinated oil, probably containing the chlor compounds $C_6H_{10}Cl_2$ and $C_9H_{14}Cl_2$. By careful addition of alcoholic potassic hydrate it is converted into the above oxides, which are then separated by fractional distillation.

Compounds of the Acetone Radicals with other Elements.

445. *Dimethyl carbon-dichloride*, or *methyl chlor-acetol*:

$$CH_3.CCl_2.CH_3,$$

is formed by the action of phosphoric chloride on acetone:

$$(CH_3)_2CO + PCl_5 = (CH_3)_2CCl_2 + POCl_3,$$

as a colourless, mobile liquid, boiling at 69°–70°, and which is isomeric with propylidene dichloride, $CH_3.CH_2.CHCl_2$, boiling at 84°–87°. By alcoholic potassic hydrate it is converted into monochlor propylene (see this):

$$CH_3.CCl_2.CH_3 + KOH = CH_3.CCl{:}CH_2 + KCl + H_2O,$$

which is formed also in large quantity in the preparation of the dichloride, hydrochloric acid being evolved:

$$CH_3.CO.CH_3 + PCl_5 = POCl_3 + HCl + CH_3.CCl{:}CH_2.$$

The corresponding *dimethyl carbon-dibromide*, or *methyl brom-acetol*, $CH_3.CBr_2.CH_3$, prepared from acetone and phosphoric chloro-bromide:

$$(CH_3)_2CO + PCl_3Br_2 = POCl_3 + (CH_3)_2CBr_2,$$

boils between 113° and 116°, and has at 0° sp. gr. 1·815.

446. *Thiacetone* is obtained as the doubled molecule, $C_6H_{12}S_2$ =  $\frac{CH_3}{CH_3}>C<\frac{S}{S}>C<\frac{CH_3}{CH_3}$, on bringing together the higher sulphides of phosphorus and acetone. The reaction:

$$2P_2S_5 + 10C_3H_6O = 2P_2O_5 + 5(C_3H_6)_2S_2,$$

which, however, is accompanied by other processes, evolves much heat. By fractional distillation the double thiacetone is obtained as a yellowish oil of extremely unpleasant and persistent odour. It boils between 183° and 185°, and has the vapour density 5·08.

447. On allowing acetone saturated with ammonia gas to stand some time, as by heating the mixture to 100° in sealed tubes, various basic nitrogen compounds are obtained, which probably possess some similarity with the aldehyde derivatives obtained in analogous manner, but require closer investigation.

An acetone solution containing hydrocyanic acid is converted on heating with hydrochloric acid into *a-oxyisobutyric acid* (see this). The reaction completely corresponds with the conversion of aldehydes into acids of the lactic series.

448. Numerous halogen substitution products of acetone are known: *monochlor acetone*, C_3H_5ClO or $CH_3.CO.CH_2Cl$, and two isomeric dichlor acetones, $CH_3.CO.CHCl_2$ and $CH_2Cl.CO.CH_2Cl$; a trichlor acetone, $C_3H_3Cl_3O_3$; tetrachlor acetone, $C_3H_2.Cl_4O$; pentachlor acetone, $CHCl_2.CO.CCl_3$; and perchlor acetone, $CCl_3.CO.CCl_3$. They are all liquids of powerfully irritating odour. From acetone itself only the first four are prepared, the two latter being obtained from other organic compounds, such as citric acid. The more interesting of them will be described later. Some bromine and iodine substitution products of acetone are also known.

Homologues of Acetone.

449. The formula C_4H_8O only corresponds to a single ketone, that isomeric with butyric aldehyde, *methyl-ethyl ketone*:

$$CH_3.CO.CH_2.CH_3,$$

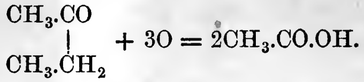
which is obtained by oxidation of secondary butylic alcohol (§ 169). It is also obtained by double decomposition of acetic chloride and zinc ethyl:

$$2CH_3.COCl + Zn(C_2H_5)_2 = ZnCl_2 + 2CH_3.CO.C_2H_5,$$

as also by boiling ethylic methyl aceto-acetate with an alkali:

$$CH_3.CO.CH.(CH_3).CO.O.C_2H_5 + 2KOH = K_2CO_3 + HO.C_2H_5 \\ + CH_3.CO.CH_2.CH_3,$$

and is contained in small quantity in the crude acetone prepared from acetates. Methyl-ethyl ketone is a colourless liquid of agreeable odour, of sp. gr. ·8125, which boils at 81°. On oxidation it yields only acetic acid:



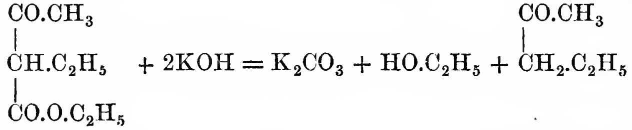
$$\begin{array}{l}CH_3.CO\\ \quad| \\ CH_3.CH_2\end{array} + 3O = 2CH_3.CO.OH.$$

450. Three isomeric ketones, $C_5H_{10}O$, correspond to valeric aldehyde.

1. *Methyl-propyl ketone*, $CH_3.CO.CH_2.CH_2.CH_3$, is obtained by dry distillation of a mixture of an acetate and butyrate:

$$CH_3.CO.OM + CH_3.CH_2.CH_2.CO.OM = M_2CO_3 \\ + CH_3.CO.CH_2.CH_2.CH_3;$$

also obtained on the careful oxidation of propyl-methyl carbinol, into which it is converted by action of nascent hydrogen (§ 170), and also formed by the decomposition of ethylic ethyl aceto-acetate by potassic hydrate:



$$\begin{array}{l}CO.CH_3\\ |\\ CH.C_2H_5\\ |\\ CO.O.C_2H_5\end{array} + 2KOH = K_2CO_3 + HO.C_2H_5 + \begin{array}{l}CO.CH_3\\ |\\ CH_2.C_2H_5\end{array}$$

It is a colourless liquid, of agreeable acetone-like smell, which at 13° has sp. gr. ·8132 and boils at 101°. It yields a beautifully crystalline compound with hydric sodic sulphite. By oxidation it gives acetic and propionic acids.

2. *Methyl-isopropyl ketone*, $CH_3.CO.CH{<}\begin{smallmatrix}CH_3\\ CH_3\end{smallmatrix}$, is obtained by the decomposition of ethylic dimethyl aceto-acetate:

$$CH_3.CO.C(CH_3)_2.CO.O.C_2H_5.$$

It boils at 93·5°, and has at 13° the sp. gr. ·8099.

3. *Diethyl ketone*, or *propione*, $CH_3.CH_2.CO.CH_2.CH_3$, is obtained by the dry distillation of propionates:

$$(C_2H_5.CO.O)_2Ca = CO_3Ca + (C_2H_5)_2CO;$$

by decomposition of propionic chloride by zinc ethyl:

$$2C_2H_5.CO.Cl + Zn(C_2H_5)_2 = ZnCl_2 + 2C_2H_5.CO.C_2H_5;$$

and by the action of carbonic oxide on the product, containing potassium ethyl, of the action of potassium on zinc ethyl:

$$CO + 2K.C_2H_5 = K_2 + CO.(C_2H_5)_2.$$

It is also prepared by the careful oxidation of diethoxalic acid:

$$\begin{smallmatrix}C_2H_5\\ C_2H_5\end{smallmatrix}{>}C.OH.CO.OH + O = \begin{smallmatrix}C_2H_5\\ C_2H_5\end{smallmatrix}{>}CO + H_2O + CO_2.$$

It has sp. gr. ·813 at 20°, and boils at 101°. It is converted into propionic and acetic acids on energetic oxidation. It gives no compounds with the hydric sulphites.

451. Hex-carbon ketones, $C_6H_{12}O$. Six of these bodies are possible—namely, four methyl-butyl ketones, $CH_3.CO.C_4H_9$, and two ethyl-propyl ketones, $C_2H_5.CO.C_3H_7$.

Methyl-butyl ketone, $CH_3.CO.CH_2.CH_2.CH_2.CH_3$, is obtained by the oxidation of methyl-butyl carbinol (§ 171). It boils at 127° and has sp. gr. ·8298.

Methyl-trimethyl carbin-ketone, pinacoline, $CH_3.CO.C(CH_3)_3$, is prepared by heating pinacone with dilute sulphuric acid or with concentrated acĕtic acid. It is a colourless oil, boiling at 105°; on oxidation it yields trimethacetic acid; nascent hydrogen converts it into *pinacoline alcohol,* $C_6H_{13}.OH$.

A ketone of this formula, boiling at 128°, is obtained as a bye product in the dry distillation of calcic butyrate. It has at 0° sp. gr. ·833, and is probably *ethyl-propyl ketone :*

$$CH_3.CH_2.CO.CH_2.CH_2.CH_3.$$

452. The main product of the dry distillation of calcic butyrate is *dipropyl ketone,* or *butyrone,* $C_7H_{14}O = (CH_3.CH_2.CH_2)_2CO$. It boils at 144°–145°, and has at 20° the sp. gr. ·82. By chromic acid and sulphuric acid it is oxidised to butyric and propionic acids, by fuming nitric acid to nitro-propionic acid, $C_3H_5(NO_2)O_2$.

Diisopropyl ketone, or *isobutyrone,* $[(CH_3)_2.CH]_2CO$, is obtained by the careful oxidation of diisopropyl oxalic acid and by the dry distillation of calcic isobutyrate. It distils at 123°–125°, and is oxidised by chromic acid to isobutyric, acetic, and carbonic acids.

Methyl-amyl ketone, $CH_3.CO.CH_2.CH_2.CH_2.CH_2.CH_3$, is obtained by the oxidation of methyl-amyl carbinol, as an agreeable-smelling liquid, boiling at 155°–156°, which unites with the alkaline hydric sulphites and is oxidised to acetic and normal valeric acids.

Methyl-isoamyl ketone, $CH_3.CO.CH_2.CH_2.CH:(CH_3)_2$, is obtained by the action of zinc amyl on acetic chloride or of isocaproic chloride on zinc methyl:

$$2CH_3.CO.Cl + Zn[CH_2.CH_2.CH:(CH_3)_2]_2$$
$$= ZnCl_2 + 2CH_3.CO.CH_2.CH_2.CH:(CH_3)_2$$
$$(CH_3)_2Zn + 2Cl.CO.CH_2.CH_2.CH:(CH_3)_2$$
$$= ZnCl_2 + 2CH_3.CO.CH_2.CH_2.CH:(CH_3)_2.$$

It boils at 144° and has at 0° sp. gr. ·829. It unites with hydric sulphites, and yields acetic and isovaleric acid on oxidation.

453. *Methyl-hexyl ketone,* or *methyl œnanthone,* $C_8H_{16}O$ or $CH_3.CO.CH_2.CH_2.CH_2.CH_2.CH_2.CH_3$, is obtained by dry distillation of a mixture of calcic acetate and œnanthate, and by the oxidation of methyl-hexyl carbinol (§ 173). It boils at 171° and yields on oxidation acetic and caproic acids. The sp. gr. = ·818.

An isomeric ketone, termed *methyl butyrone,* occurs amongst the bye products of the preparation of butyrone, as a liquid boiling at 180°. It is probably a *propyl-butyl ketone,* $C_3H_7.CO.C_4H_9$.

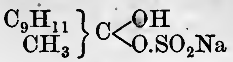
454. The body termed *valerone,* obtained by the dry distillation of calcic isovalerate, is undoubtedly *diisobutyl ketone :*

$$[(CH_3)_2.CH.CH_2]_2CO.$$

It is an oily liquid, boiling at 181°–182°, and of sp. gr. ·823 at 20°.

454*a*. *Methyl-octyl ketone,* $CH_3.CO.CH_2.C_7H_{15}$, is prepared by the action of alcoholic potash on ethyl-heptyl aceto-acetate. It is a liquid boiling at 214° and of sp. gr. ·8294 at 17·7°.

455. *Methyl-nonyl ketone,* $C_{11}H_{22}O = CH_3.CO.C_9H_{19}$, forms the main constituent of ethereal oil of rue (*Ruta graveolens*), and is obtained therefrom by shaking with a concentrated solution of hydric sodic sulphite in form of the crystalline compound



$$\left.\begin{matrix} C_9H_{11} \\ CH_3 \end{matrix}\right\} C \begin{matrix} \diagup OH \\ \diagdown O.SO_2Na \end{matrix}$$

from which it is obtained in the free state by treatment with alkaline carbonates. It is also obtained by the dry distillation of a mixture of calcic acetate and caproate. At ordinary temperatures it is a colourless oil with blue fluorescence, of sp. gr. ·8268, which, on cooling, solidifies in leafy crystals; it melts at + 15°, and boils at 225°–226°.

Isomeric with this is *caprone*, probably *normal diamyl ketone*, $(C_5H_{11})_2:CO$, obtained by the dry distillation of calcic caproate. It boils at 220°–221°, has at 0° sp. gr. ·822, and solidifies to a crystalline mass on cooling.

Œnanthone, $C_{13}H_{26}O = (C_6H_{13})_2O$, is a *dihexyl ketone*, which is obtained by the dry distillation of potassic œnanthate. It crystallises in leafy crystals, melting at 30°, of sp. gr. ·824, which boil at 254°–255°.

455*a*. Isomeric with this is *methyl-undecyl ketone :*

$$CH_3.CO.C_{11}H_{23},$$

prepared by the dry distillation of a mixture of baric laurate and acetate under reduced pressure. It melts at 28°, boils at 195·5° under 100 mm. pressure and at 263° at ordinary atmospheric pressure.

Baric caprylate yields on decomposition, at high temperatures, a *diheptyl ketone*, $C_{15}H_{30}O = (C_7H_{15})_2CO$. It crystallises in leafy crystals, melts at 40°, and boils at 278°.

455*b*. The isomeric *methyl-tridecyl ketone :*

$$C_{15}H_{30}O = CH_3.CO.C_{13}H_{27},$$

is prepared by the dry distillation of a mixture of baric myristate and acetate under reduced pressure. It melts at 39°, boils at 223·5° under 110 mm. pressure and at 294° under normal pressure.

455*c*. *Methyl-pentadecyl ketone*, $C_{17}H_{34}O = CH_3.CO.C_{15}H_{31}$, obtained on dry distillation of mixed acetate and palmitate of barium under reduced pressure, melts at 48°, boils at 246° under 110 mm. pressure and at 319°–320° under atmospheric pressure.

Methyl-diheptyl-carbin-ketone, $CH_3.CO.C(C_7H_{15})_2$, isomeric with the preceding, is obtained by the action of alcoholic potash on ethylic diheptyl aceto-acetate; it is a colourless liquid, boiling at 300°–304°, and of sp. gr. ·826 at 17°.

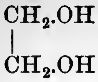
455*d*. *Methyl-heptadecyl ketone*, $C_{19}H_{38}O = CH_3.CO.C_{17}H_{35}$, prepared as above from baric stearate and acetate, melts at 55·5°, and boils at 266·5° under 110° mm. pressure.

GLYCOL DERIVATIVES.

Compounds of the Diad Alcohol Radicals, C_nH_{2n}.

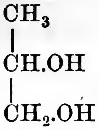
456. By replacement of two of the hydrogen atoms of a paraffin on two different carbon atoms there results derivatives of the divalent alcohol radicals, C_nH_{2n}, the olefines, whose chief representatives are the hydrates, the diacid alcohols or glycols, $C_nH_{2n}(OH)_2$.

The first member of the series must be a dicarbonide, ethylene glycol, $C_2H_4(OH)_2$, a double primary diacid alcohol:



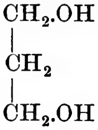
$$\begin{array}{c} \mathrm{CH_2.OH} \\ | \\ \mathrm{CH_2.OH} \end{array}$$

The second member, $C_3H_6(OH)_2$, is known in two isomers, of which the one is a primary-secondary, the other a diprimary, glycol:



$$\begin{array}{c} \mathrm{CH_3} \\ | \\ \mathrm{CH.OH} \\ | \\ \mathrm{CH_2.OH} \end{array}$$

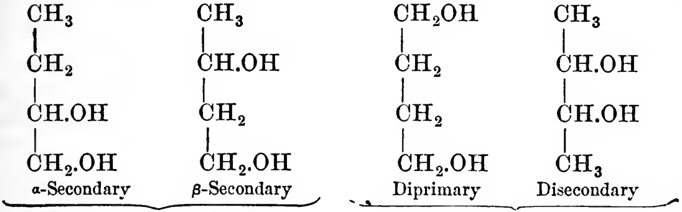
and



$$\begin{array}{c} \mathrm{CH_2.OH} \\ | \\ \mathrm{CH_2} \\ | \\ \mathrm{CH_2.OH} \end{array}$$

Propylene glycol. Trimethene glycol.

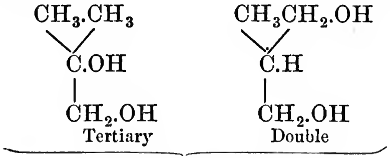
Of the tetracarbon glycol, $C_4H_8(OH)_2$, six isomers are possible, namely:



$$\begin{array}{cccc} \mathrm{CH_3} & \mathrm{CH_3} & \mathrm{CH_2OH} & \mathrm{CH_3} \\ | & | & | & | \\ \mathrm{CH_2} & \mathrm{CH.OH} & \mathrm{CH_2} & \mathrm{CH.OH} \\ | & | & | & | \\ \mathrm{CH.OH} & \mathrm{CH_2} & \mathrm{CH_2} & \mathrm{CH.OH} \\ | & | & | & | \\ \mathrm{CH_2.OH} & \mathrm{CH_2.OH} & \mathrm{CH_2.OH} & \mathrm{CH_3} \end{array}$$

α-Secondary β-Secondary Diprimary Disecondary

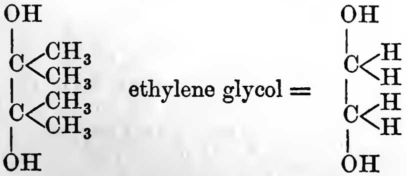
Primary butylene glycol. Butylene glycol.



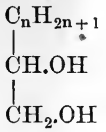
Tertiary Double

Primary isobutylene glycol.

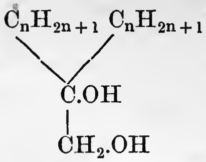
It is self-evident that for every additional carbon atom the number of possible isomers must increase in rapid progression, and that still further complications in the character of the substitution must ensue, as, for instance, secondary-tertiary glycols. Of the ditertiary the first member, the hexcarbon acetone-pinacone or tetramethylethylene glycol, is known:



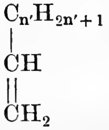
457. In by far the largest number of known glycols one of the hydroxyl groups occupies the primary position, i.e. is on a terminal carbon atom, the other on the next neighbouring, either secondarily or tertiarily united, carbon atom. These are the primary α-secondary and primary α-tertiary glycols:



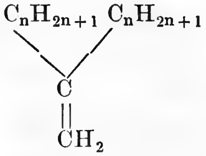
$$\begin{array}{l} C_nH_{2n+1} \\ | \\ CH.OH \\ | \\ CH_2.OH \end{array}$$

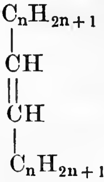


In those cases where the hydroxyl groups are united to neighbouring carbon atoms the hydrocarbon radicals of the glycols can form free molecules by diad carbon union:



$$\begin{array}{l} C_{n'}H_{2n'+1} \\ | \\ CH \\ \| \\ CH_2 \end{array}$$





$$\begin{array}{l} C_nH_{2n+1} \\ | \\ CH \\ \| \\ CH \\ | \\ C_nH_{2n+1} \end{array}$$

&c.

These hydrocarbons (olefines) all contain twice as many atoms of hydrogen as of carbon, have all with different molecular weights the same percentage composition, and are polymeric to the simplest atomic proportion formula, CH_2.

Olefines.

Hydrocarbons of the Formula C_nH_{2n}.

458. For the preparation of the olefines the mono-acid alcohols or their haloid compounds are usually employed.

From the alcohol molecules a molecule of water must be removed. This occurs on heating with strong polybasic acids, such as sulphuric acid, or with certain salts, such as zincic chloride. The higher molecular alcohols, which cannot be distilled unchanged, are resolved on heating alone—by distillation—into water and olefine.

By employment of sulphuric acid as the decomposing agent there is first formed, in addition to water, hydric alkyl sulphate, which at higher temperature splits into olefine and sulphuric acid:

$$C_nH_{2n+1}.H.SO_4 = C_nH_{2n} + H_2SO_4 \text{ (§ 215).}$$

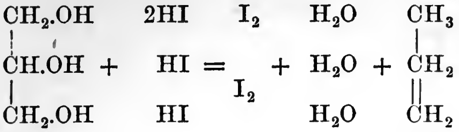
As the latter is regenerated, the process (similarly to that of the formation of ether, § 201) can be made continuous. For this purpose the sulphuric acid is heated to the temperature of decomposition of the monalkyl sulphate, and the supply of the alcohol or its vapour so regulated that the temperature remains constant at that point.

The secondary and tertiary alcohols are most readily decomposed in this way (that is, at the relatively lowest temperatures).

If the alkyl haloids be employed as the raw material for the preparation of olefines, the decomposition is effected by means of alcoholic potassic hydrate. The potassium unites with the halogen, whilst the hydroxyl residue of the base removes a hydrogen atom from the neighbouring carbon atom, and double carbon linking then ensues:

$$C_nH_{2n+1}I + KOH = KI + H_2O + C_nH_{2n}.$$

459. Tri- and polyvalent alcohols yield olefines when heated with adequate quantities of sufficiently concentrated hydriodic acid:



$$\begin{array}{lcccccccl}
CH_2.OH & & 2HI & & I_2 & & H_2O & & CH_3 \\
| & & & & & & & & | \\
CH.OH & + & HI & = & & + & H_2O & + & CH_2 \\
| & & & & I_2 & & & & \| \\
CH_2.OH & & HI & & & & H_2O & & CH_2
\end{array}$$

Glycerine. Propylene.

Olefines with $_{n'}$ carbon atoms are obtained from the monobasic organic acids of the formula $C_nH_{2n}O_2$ or $C_{n'}H_{2n'+1}.OH$ when their salts are mixed with soda lime and submitted to dry distillation; not only paraffins being formed (§ 149), but also hydrogen and olefines:

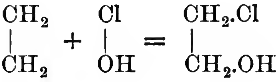
$$C_{n'}H_{2n'+1}.CO.ONa + HONa = CO(ONa)_2 + H_2 + C_{n'}H_{2n'}.$$

Single olefines, especially the first members of the series, occur amongst the products of the dry distillation of complex organic bodies. Lighting gas, prepared from wood or coal, invariably contains some quantity of ethylene, C_2H_4.

460. The true olefines invariably unite with free halogens when brought into contact, with change of the divalent union of the carbon atoms into monovalent, and formation of the olefine dihaloids. As these do not mix with water, and otherwise resemble oils, ethylene received the name olefiant gas, and the whole group of hydrocarbons are termed olefines.

The property of direct union with halogens is general to molecules with other than single carbon union.

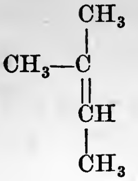
Similarly to their behaviour with halogens, the olefines also unite with the elements of hypochlorous acid, with formation of olefine haloid hydrates:



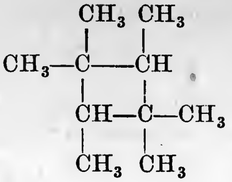
$$\begin{array}{ccccl}
CH_2 & & Cl & & CH_2.Cl \\
| & + & | & = & | \\
CH_2 & & OH & & CH_2.OH
\end{array}$$

That olefines unite with concentrated sulphuric acid to form monalkyl sulphates, and with haloid hydro-acids to form alkyl haloids, has been already mentioned (§ 163), as also the fact, in the case of olefines containing more than two carbon atoms, that the bodies so formed are derivatives of secondary or tertiary alcohols.

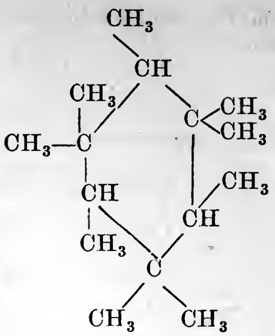
461. All olefines have the property of polymerising at the moment of their formation, their nascent bonds, instead of uniting to divalent linking, combining with those of similar molecules, and so yielding bodies in which closed rings must exist. In the simplest cases two olefine molecules unite together, but the polymerisation can go much further. In the preparation of isoamylene from isoamylic alcohol, diisoamylene and triisoamylene are invariably formed. Their formation may be explained as follows:



Isoamylene.



Diisoamylene.

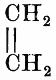


Triisoamylene.

These polymers have been mostly but little investigated. Their general molecular formula is evidently the same as that of the olefines:

$$a.C_{n'}H_{2n'} = C_nH_{2n}, \text{ if } a.n' = n.$$

They differ frequently in their properties from the simple olefines.



Ethylene, $C_2H_4 = \begin{array}{c}CH_2\\ \| \\ CH_2\end{array}$

462. The first member of the series is *ethylene*, also termed *ethene* or *olefiant gas*, as the property of yielding an oily body with chlorine was first discovered in its case.

It is dimethene, and results therefore from the halogen derivatives of methene on removing the halogen from them by metals:

$$2CH_2.I_2 + 2Na_2 = 4NaI + CH_2:CH_2.$$

Similarly it is formed from methylic alcohol on heating with phosphoric anhydride, the two methene groups in the nascent state uniting to an ethylene molecule.

It is obtained by the dry distillation of many organic substances, such as fats, resins, coal, wood, &c.; in small quantity also by the distillation of salts of organic acids, even those of formic acid. Synthetically it can be prepared, together with methane, by passing a mixture of the vapour of carbonic disulphide and sulphuretted hydrogen gas over heated copper:

$$2CS_2 + 2H_2S + 12Cu = 6Cu_2S + C_2H_4.$$

It is most conveniently prepared by heating ethylic alcohol with sulphuric acid or boric anhydride. By employment of the first the process can be made continuous, the method being as follows:—

A mixture of twenty-five grams alcohol with 150 grams of concentrated sulphuric acid is placed in a flask of two to three litres' capacity, which is placed on a sand bath and connected to a series of four Woulff's bottles, of which the first serves to collect the condensed liquid distillate; the second contains concentrated sulphuric acid; the third and fourth are about half filled with concentrated potassic hydrate solution, to absorb any acid gases (SO_2 and CO_2). The flask is now heated till ethylene is quietly evolved, and a cooled mixture of equal parts of ethylic alcohol and concentrated acid is then allowed to flow drop by drop down the funnel tube placed in the neck of the flask. By regulating the rapidity of the flow and the flame, a continuous evolution of ethylene is obtained, which may be passed from the last Woulff's bottle into a gas holder, or into the halogen directly, if required, for the preparation of ethylene dihaloids.

463. Ethylene is a colourless gas of peculiar agreeable odour, which burns in air with a clear luminous flame. Its density is ·9784. At 0° and under a pressure of 42° atmospheres it condenses to a mobile, colourless liquid.

Water absorbs about $\frac{1}{8}$ volume, alcohol and ether about two volumes, of the gas. Ethylene unites directly and readily with chlorine, bromine, and iodine, to form dihaloids; it is also absorbed by concentrated sulphuric acid, especially on slight warming, hydric ethylic sulphate being formed :

$$CH_2:CH_2 + H_2SO_4 = (CH_3.CH_2)HSO_4,$$

from which, by distillation with water, ethylic alcohol can be regenerated. It is absorbed with much greater readiness by Nordhausen sulphuric acid, yielding with the SO_3 ethionic anhydride (§ 513).

It is also absorbed by concentrated hydriodic acid, especially on gentle heating, ethylic iodide being formed :

$$CH_2:CH_2 + HI = CH_3.CH_2I.$$

At a red heat it is decomposed, yielding methane and tarry products.

464. *Polymerisation of Ethylene.*—In the distillation of ethylene, polymeric products are always formed, though but in small quantity. These are more abundantly obtained by the dry distillation of metallic ethylic sulphates. Together with ethylene :

$$K.C_2H_5.SO_4 = KHSO_4 + C_2H_4,$$

condensable vapours pass over, which collect in a cooled receiver to a liquid of acid reaction. On treatment with water, an oil separates, from which on strong cooling a solid hydrocarbon—*etherine*—crystallises, which melts at 110° and boils at 260°. The portion remaining liquid is termed *etherol.* Both bodies have the percentage composition of olefines and the formula C_nH_{2n}.

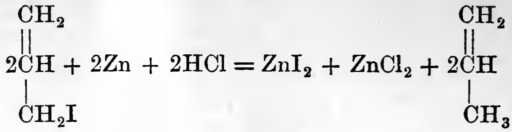
Propylene, $C_3H_6 = CH_3.CH:CH_2$.

465. Propylene is frequently observed amongst the products of the dry distillation of organic bodies. It is formed, e.g., when the vapour of isoamylic alcohol is passed through red-hot tubes and by the dry distillation of the salts of many acids of the formula $C_nH_{2n}O_2$. Isopropylic iodide is converted into propylene by alcoholic potassic hydrate even at 40°–50° :

$$CH_3.CHI.CH_3 + KOH = KI + H_2O + CH_3.CH:CH_2.$$

Primary propylic iodide suffers the same decomposition, only with greater difficulty.

Propylene is further obtained by the action of phosphorous iodide or hydriodic acid upon glycerine (§ 459). Nearly pure it is obtained with greatest readiness when allylic iodide is treated with zinc and hydrochloric acid in the presence of alcohol:



$$\begin{array}{l}CH_2\\ \|\\ 2CH\\ |\\ CH_2I\end{array} + 2Zn + 2HCl = ZnI_2 + ZnCl_2 + \begin{array}{l}CH_2\\ \|\\ 2CH\\ |\\ CH_3\end{array}$$

Propylene is a gas very similar to ethylene, and of the density 1·498. It is liquefied on great compression. It is readily absorbed by concentrated sulphuric acid in the cold, yielding isopropylic hydric sulphate, which even at ordinary temperatures soon decomposes into sulphuric acid and polymeric propylenes.

It yields isopropylic iodide directly with concentrated hydriodic acid, and isopropylic chloride by long heating with hydrochloric acid.

Butylenes, C_4H_8.

466. The two tetracarbon nuclei admit of three butylenes.

1. *Normal butylene*, $CH_3.CH_2.CH{:}CH_2$, is obtained as methyl allyl by heating a mixture of methylic and allylic iodides diluted with ether and metallic sodium at 100° in strong closed vessels:

$$CH_3I + I.CH_2.CH{:}CH_2 + Na_2 = 2NaI + CH_3.CH_2.CH{:}CH_2.$$

The cooled vessel is surrounded with a freezing mixture, opened, and the butylene by gentle heating distilled over into receivers cooled to at least $-10°$. It is then obtained in the form of a light, mobile, colourless liquid, which distils at about $-4°$. It unites with hydriodic acid to form secondary butylic iodide.

The same butylene is also obtained by the action of zinc ethyl on monobrom-ethylene:

$$Zn(C_2H_5)_2 + 2BrCH{:}CH_2 = ZnBr_2 + 2C_2H_5.CH{:}CH_2,$$

and by the decomposition of primary butylic iodide by potassic hydrate. It boils at $-$ 5°.

2. *Isobutylene*, $\begin{smallmatrix}CH_3\\ CH_3\end{smallmatrix}\!\!>\!C{=}CH_2$, is obtained by several methods. Isobutyl alcohol and trimethyl carbinol both yield it on treatment with sulphuric acid or zincic chloride, a great part, however, polymerising. It is more generally prepared by decomposition of isobutylic iodide or trimethyl carbin-iodide (§ 193) with alcoholic potassic hydrate:

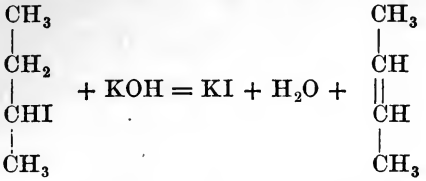
$$(CH_3)_2CH.CH_2I + KOH = KI + H_2O + (CH_3)_2{:}C{=}CH_2$$
$$(CH_3)_2CI.CH_3 + KOH = KI + H_2O + (CH_3)_2{:}C{=}CH_2.$$

It is also obtained when the vapour of isoamylic alcohol is passed through red-hot tubes, and, together with hydrogen and diisobutyl, by the electrolysis of aqueous solutions of alkaline valerates.

It is an unpleasant-smelling gas, which condenses, on cooling with a mixture of ice and salt, to a colourless liquid boiling at $-$ 7° to $-$ 6°.

It unites readily with hydriodic acid, forming trimethyl carbin-iodide. It is absorbed by a mixture of three parts of concentrated sulphuric acid and one part of water, giving hydric trimethyl carbinsulphate, which, after dilution with much water, yields trimethyl carbinol on distillation (§ 169). At the same time a considerable portion of the isobutylene polymerises, separating even during the absorption of the gas as a colourless oil, which consists in great part of triisobutylene, $C_{12}H_{24}$, boiling at 173°–176°.

3. *Pseudobutylene* is formed by heating secondary butylic iodide with alcoholic potassic hydrate :



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

and by heating the vapour of normal secondary butylic alcohol to 250°.

It is liquid at 0°, boils at + 3°, and on strong cooling crystallises. It unites with hydriodic acid to form secondary butylic iodide.

Amylenes, C_5H_{10}.

467. Of the five possible hydrocarbons of the amylene formula in which two neighbouring carbon atoms are doubly united, only four have yet been obtained, and in part still require investigation.

1. *Normal amylene*, or *ethyl-allyl*, $CH_3.CH_2.CH_2.CH:CH_2$, is obtained by the action of sodium on a mixture of ethylic and allylic iodides :

$$CH_3.CH_2I + ICH_2.CH:CH_2 + Na_2 = 2NaI$$
$$+ CH_3.CH_2.CH_2.CH:CH_2.$$

It is a colourless liquid, boiling at 73°, which gives with hydriodic acid first normal secondary amylic iodide (§ 194), and unites with hydrochloric acid, apparently only in the warm, to the corresponding first normal secondary amylic chloride. Normal amylene occurs in the fraction distilling between 30°–40° of the products of the dry distillation of some asphalts.

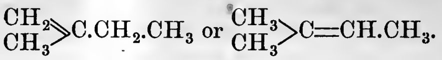
2. *Isoamylene*, $\begin{matrix}CH_3\\ CH_3\end{matrix}\!\!>C:CH.CH_3$, is formed, together with its polymers, by the distillation of isoamylic alcohol with zincic chloride, as a mobile, colourless oil of peculiar odour, of 35° boiling point and ·663 sp. gr. at 0°. It combines, even in the cold, with hydrochloric acid to secondary isoamylic chloride, with hydriodic acid to the corresponding iodide (§ 194).

It is converted nearly completely into its polymers by contact with concentrated sulphuric acid, or by action of zincic chloride on heating; dilute sulphuric acid partly producing this change, partly forming secondary isoamylic hydric sulphate.

Diamylene, $C_{10}H_{20}$, is an oil boiling at 165° and of ·777 sp. gr., which unites with two atoms of bromine to form $C_{10}H_{20}Br_2$. *Triamylene*, $C_{15}H_{30} = (C_5H_{10})_3$, distils at 248°; *tetramylene*, $C_{20}H_{40} = (C_5H_{10})_4$, at above 390°.

3. An amylene also boiling at 35°, but differing from the foregoing, is obtained from the iodide of tertiary amylic alcohol (§ 170, 6)

by decomposition with alcoholic potassic hydrate. Its odour is different to that of isoamylene, and by union with hydrochloric acid it is reconverted into tertiary amylic iodide. It is, therefore, either



$$\begin{matrix}CH_2\\CH_3\end{matrix}\!\!>C.CH_2.CH_3 \text{ or } \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C{=}CH.CH_3.$$

Probably it has the first formula, as the second agrees more with the properties of the former isomer.

4. An amylene boiling at 25° :

$$\left(\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH.CH:CH_2\,?\right),$$

is obtained from the optically inactive isoamylic iodide by action of alcoholic potassic hydrate, which appears to yield tertiary isoamylic chloride with hydrochloric acid.

5. *Methyl-ethyl ethene*, $CH_3.CH:CH.CH_2.CH_3$, is obtained by the action of potassic hydrate on the iodide from diethyl carbinol. It boils at 36°.

The amylene obtained by heating zinc ethyl with chloroform :

$$CHCl_3 + Zn(C_2H_5)_2 = ZnCl_2 + HCl + C_5H_{10},$$

requires further investigation.

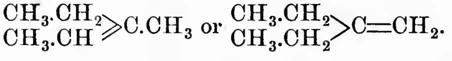
Hexylenes, C_6H_{12}.

468. Several olefines of this formula have been prepared, but scarcely enough investigated to enable rational formulæ to be assigned to them with certainty. Two isomeric hexylenes occur in the products of dry distillation of certain asphalts, which—the one in the cold, the other only on heating—unite with hydrochloric acid to form two different chlorides, $C_6H_{13}Cl$ (boiling points 115°–117° and 122°–124°).

Normal primary hexylic iodide gives with alcoholic potassic hydrate α-hexylene, boiling at 68°–70°, probably $CH_3.CH_2.CH_2.CH_2.CH:CH_2$.

The best known hexylene is obtained by decomposing first normal secondary hexylic iodide (§ 195) with alcoholic potassic hydrate. It is also derived from normal hexane, and is probably β-hexylene, $CH_3.CH_2.CH_2.CH:CH.CH_3$. Its boiling point is 65°–66°. With hydriodic acid it yields secondary hexylic iodide.

Another hexylene, boiling between 68° and 72°, is obtained by action of alcoholic potassic hydrate on the iodide of diethyl-methyl carbinol (§ 171, 6). Its constitution is expressed by one of the two formulæ :



$$\begin{matrix}CH_3.CH_2\\CH_3.CH\end{matrix}\!\!>C.CH_3 \text{ or } \begin{matrix}CH_3.CH_2\\CH_3.CH_2\end{matrix}\!\!>C{=}CH_2.$$

Hexylenes from other sources, as by decomposition of dichlorinated petroleum hexane by sodium, or by the action of high temperatures on paraffin, &c., may be passed over here, not having been sufficiently investigated.

469. Several of the higher members of the olefine group, exclusive of the above-mentioned olefines, have been obtained. From such of the monovalent alcohols as distil unchanged they are generally prepared by heating with sulphuric acid or by decomposing the corresponding haloid compounds by alcoholic potassic hydrate. By the second method a heptylene, probably $(CH_3)_2C:CH.CH(CH_3)_2$, has been obtained from the iodide derived from dimethyl-isobutyl carbinol.

It boils at 83°–84° and has sp. gr. ·714 at 0°. And by the first method *a*-normal secondary octylic alcohol (caprylic alcohol, from castor oil) yields an octylene, caprylene, which boils at 118°–119°. The higher molecular alcohols which cannot be volatilised unchanged decompose, on dry distillation, into water and hydrocarbons of the formula C_nH_{2n}. Cetylic alcohol thus yields cetene, $C_{16}H_{32}$, a liquid boiling at 275 degrees. Cerotone, $C_{27}H_{54}$, and melene, $C_{30}H_{60}$, are crystalline bodies, which readily decompose further on heating, and are therefore scarcely obtainable in the pure state. Paraffin (§ 159) in all probability contains, together with high molecular paraffins, also some quantity of hydrocarbons of the formula C_nH_{2n}. Such bodies also occur in different natural paraffin-like bodies, e.g. in ozocerite.

Halogen Compounds of the Divalent Alcohol Radicals.

470. The hydrocarbons C_nH_{2n}, existing as free molecules by the diad union of neighbouring carbon atoms, combine directly with two halogen atoms to form liquid or solid dihaloids insoluble in water. The respective bromides and chlorides of low molecular weight distil unchanged; the higher members decompose, at least partly, on heating, with evolution of the hydro-acids, and probably, in the first place, formation of halogen mono-substituted olefines:

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

The few iodides known are unstable bodies, which cannot be volatilised without partial dissociation into their components.

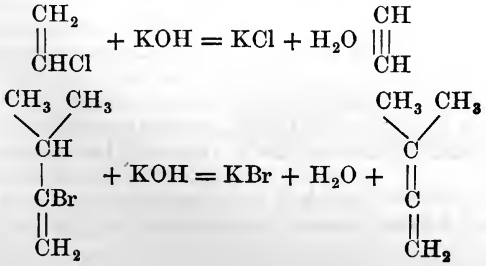
471. By action of alkaline hydrates, best in alcoholic solution, these halogen compounds cannot be converted into the divalent alcohols; the metal of the hydrate removes one halogen atom, whilst the OH group at the same time oxidises and removes a hydrogen atom, and with renewed double linking of carbon a mono-halogenated olefine is formed:

$$C_nH_{2n}Cl_2 + KOH = KCl + H_2O + C_nH_{2n-1}Cl.$$

By employment of a large excess of alkali, or by action of sodic or potassic ethylates assisted by heating, this process is repeated, another halogen atom and hydrogen atom being removed, and a hydrocarbon of the general formula C_nH_{2n-2} formed:

$$C_nH_{2n-1}Cl + KOH = KCl + H_2O + C_nH_{2n-2},$$
$$C_nH_{2n-1}Cl + NaO.C_2H_5 = NaCl + HO.C_2H_5 + C_nH_{2n-2}.$$

In these latter either two neighbouring carbon atoms are in trivalent union, or else the double union occurs twice over:



$$\begin{array}{l} CH_2 \\ \| \\ CHCl \end{array} + KOH = KCl + H_2O \begin{array}{l} CH \\ ||| \\ CH \end{array}$$

$$\begin{array}{c} CH_3\ \ CH_3 \\ \diagdown\ \diagup \\ CH \\ | \\ CBr \\ \| \\ CH_2 \end{array} + KOH = KBr + H_2O + \begin{array}{c} CH_3\ \ CH_3 \\ \diagdown\ \diagup \\ C \\ \| \\ C \\ \| \\ CH_2 \end{array}$$

The halogenised olefines formed as the first products of the action of alkalies are themselves capable of combining with two halogen atoms, and the resulting trihaloids, $C_nH_{2n-1}Cl_3$, suffer a like decomposition with alkalies, so that in this way a gradual replacement of the hydrogen atoms of paraffins by halogens can be effected. The processes can be expressed by the following series of equations:

$C_nH_{2n+1}Br + KOH = KBr + H_2O + C_nH_{2n}$
$C_nH_{2n} + Br_2 = C_nH_{2n}Br_2$
$C_nH_{2n}Br_2 + KOH = KBr + H_2O + C_nH_{2n-1}Br$, monobrom olefine
$C_nH_{2n-1}Br + Br_2 = C_nH_{2n-1}Br_3$, tribrom paraffin
$C_nH_{2n-1}Br_3 + KOH = KBr + OH_2 + C_nH_{2n-2}Br_2$, dibrom olefine
$C_nH_{2n-2}Br_2 + Br_2 = C_nH_{2n-2}Br_4$, tetrabrom paraffin
$C_nH_{2n-2}Br_4 + KOH = KBr + KOH + C_nH_{2n-3}Br_3$, tribrom olefine
&c.

472. The olefine dihaloids can be reconverted into olefines, with partial polymerisation, by action of strongly positive metals:

$$C_nH_{2n}Cl_2 + Na_2 = 2NaCl + C_nH_{2n}.$$

By action of nascent hydrogen, best from zinc and hydrochloric acid, or by action of hydriodic acid, the olefine dihaloids are converted into paraffins (§ 149):

$$C_nH_{2n}Cl_2 + 2HCl + 2Zn = 2ZnCl_2 + C_nH_{2n+2}.$$

Ethylene Haloids.

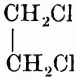
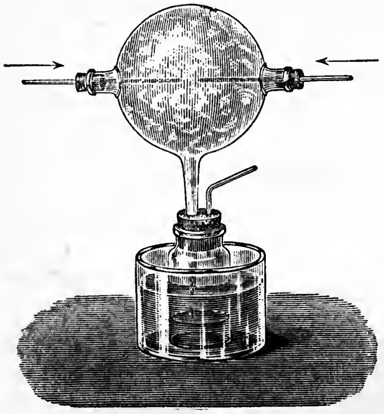
473. *Ethylene dichloride,* $C_2H_4Cl_2$ =  $\begin{array}{c}CH_2Cl\\ |\\ CH_2Cl\end{array}$, isomeric with ethylidene dichloride (§ 381). This compound was discovered in 1795 by four Dutch chemists, and was long termed *Dutch liquid,* ethylene being named *olefiant gas.* To prepare it, equal volumes of ethylene and chlorine, both quite dry, are brought together in a tritubulated balloon (fig. 21). The union is accompanied by evolution of heat, and the ethylene dichloride formed condenses on the sides of the balloon and flows down the long neck into a cooled receiver, from which any uncombined gas can escape by the exit tube.

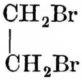
FIG. 21.



Ethylene dichloride is a colourless, mobile liquid of sweet odour, of sp. gr. 1·28 and of boiling point 85°. It is insoluble in water, but miscible in all proportions with alcohol and ether. By alcoholic potassic hydrate it is converted into monochlor ethylene, C_2H_3Cl; this by combination with chlorine yields a trichlor ethane,

$C_2H_3Cl_3$, which is not identical with that obtained by the direct chlorination of ethane. By repeated successive treatment with alcoholic potassic hydrate and union with chlorine there are formed two series of chlorinated ethylenes and ethanes, of which only the two members richest in chlorine are identical with the products of the substituting action of chlorine on ethane. The following is a tabular view of these derivatives :

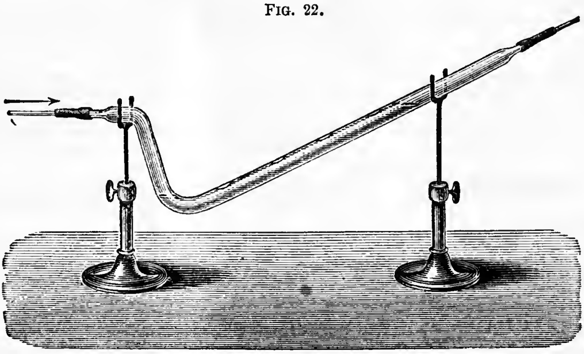
Products from Ethylene.		Products of the direct Chlorination of Ethane
By Alcoholic Potassic Hydrate	By Combination of the foregoing with Chlorine	
	$\begin{array}{l}CH_2Cl\\ \vert\\ CH_2.Cl\end{array}$ boil. point 85°	$\begin{array}{l}CH_3\\ \vert\\ CHCl_2\end{array}$ boils at 58°–59°
$\begin{array}{l}CH_2\\ \Vert\\ CHCl\end{array}$ boils at −18° Chlor ethylene	$\begin{array}{l}CH_2.Cl\\ \vert\\ CHCl_2\end{array}$ boils at 115° Chlor-ethylene dichloride	$\begin{array}{l}CH_3\\ \vert\\ CCl_3\end{array}$ boils at 75° Trichlor ethane
$\begin{array}{l}CHCl\\ \vert\\ CHCl\end{array}$ boils at + 37° Dichlor ethylene	$\begin{array}{l}CHCl_2\\ \vert\\ CHCl_2\end{array}$ boils at 137° Dichlor-ethylene dichloride	$\begin{array}{l}CH_2Cl\\ \vert\\ CCl_3\end{array}$ boils at 102° Tetrachlor ethane
$\begin{array}{l}CHCl\\ \Vert\\ CCl_2\end{array}$ boils at 88° Trichlor ethylene	$\begin{array}{l}CHCl_2\\ \vert\\ CCl_3\end{array}$ boils at 158° Trichlor-ethylene dichloride, or pentachlor ethane	
$\begin{array}{l}CCl_2\\ \Vert\\ CCl_2\end{array}$ boils at 117° Perchlor ethylene	$\begin{array}{l}CCl_3\\ \vert\\ CCl_3\end{array}$ boils at 182° Perchlor ethane	

474. *Ethylene dibromide*, $C_2H_4Br_2$ =  $\begin{array}{l}CH_2Br\\ \vert\\ CH_2Br\end{array}$, is formed, with strong evolution of heat, by bringing together bromine and ethylene gas. In order to prepare this important body, which serves as the starting point in the preparation of other ethylene derivatives, ethylene gas is absorbed by liquid bromine kept well cooled. This is frequently done in a thick flask of 2–3 litres' contents, on the bottom of which is placed 120–150 grams of bromine covered with water. The flask is then filled with olefiant gas, and, when the air has been completely expelled, closed with a cork, through which passes a tube connected with a gas holder filled with ethylene. On shaking the flask the gas is quickly absorbed by the bromine, and is constantly replenished from the store in the gas holder. Ethylene evolved in a regular stream, as in the above-given method (§ 462), can be conducted directly into liquid bromine, the only precaution requisite being that the gas remains a sufficient length of time in contact with the bromine for complete absorption. This is effected by passing the gas through the bromine contained in the long limb of the bent glass tube in fig. 22.

As soon as, by either of these methods, the bromine is nearly saturated with ethylene, shown by its being nearly decolorised, the product is shaken with dilute solution of alkali till colourless, the under layer separated from the aqueous solution, and, after mixing with concentrated sulphuric acid to fix the water, distilled on a sand bath, when pure ethylene dibromide passes over.

It is a mobile, colourless, sweet-smelling liquid of sp. gr. 2·163; it solidifies at 0° to colourless crystals, melting at + 9°. The boiling point is 129°. By alcoholic solution of potassic hydrate it is converted into monobrom ethylene, $CH_2{:}CHBr$ (boiling point 23°), from which a series of brominated ethanes and ethylenes can be prepared, similar to the chlorine derivatives (§ 473).

FIG. 22.



Ethylene dibromide can be regenerated from monobrom ethylene, by heating in closed vessels to 100°, with a solution of hydrobromic acid saturated at + 6°:

$$\begin{array}{l}CH_2\\ \|\\ CHBr\end{array} + HBr = \begin{array}{l}CH_2Br\\ |\\ CH_2Br\end{array}$$

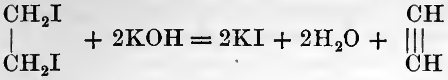
Monobrom ethylene unites more slowly, and apparently in quite a different manner, with dilute hydrobromic acid. If the acid saturated at + 6° be diluted with one-third of its volume of water, and then employed, ethylidene dibromide is the main product:

$$\begin{array}{l}CH_2\\ \|\\ CHBr\end{array} + HBr = \begin{array}{l}CH_3\\ |\\ CHBr_2\end{array}$$

475. *Ethylene diiodide*, $C_2H_4I_2 = \begin{array}{l}CH_2I\\ |\\ CH_2I\end{array}$. Ethylene unites with iodine when exposed to light or on gentle heating, especially if the iodine employed be somewhat damp. The compound is solid, crystallising in colourless silky needles or prisms, which melt at 75°, and on stronger heating decompose into ethylene and free iodine. This change also occurs at ordinary temperatures, though very slowly.

Ethylene diiodide can only be sublimed or preserved colourless in vessels filled with ethylene gas.

Alcoholic potassic hydrate decomposes ethylene diiodide very readily. Only a little moniodo-ethylene, $CH_2{:}CHI$, is obtained, as a colourless oil, boiling at 55°, the greater part being converted into acetylene, C_2H_2 :



$$\begin{array}{l} CH_2I \\ | \\ CH_2I \end{array} + 2KOH = 2KI + 2H_2O + \begin{array}{l} CH \\ ||| \\ CH \end{array}$$

476. Some double haloids of ethylene are known.

Ethylene chloro-iodide, $C_2H_4ClI = CH_2Cl.CH_2I$, can be prepared by the action of ethylene on iodine chloride, and by decomposition of ethylene diiodide with a little mercuric chloride:

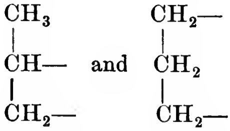
$$2C_2H_4I_2 + HgCl_2 = HgI_2 + 2C_2H_4ClI.$$

It is a heavy liquid of sweet odour, boiling at 137°–138°.

Ethylene brom-iodide, $C_2H_4BrI = CH_2Br.CH_2I$, is formed when hydriodic acid (saturated at + 4°) is heated at 100° with brominated ethylene, and when iodine bromide is saturated with olefiant gas. It is a colourless mass, melting at 28°, which boils at 163° and has sp. gr. 2·7 at + 1°.

Halogen Compounds of Propene.

477. The divalent alcohol radical C_3H_6 can possess two different constitutions, namely :

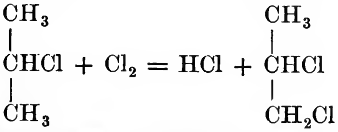


$$\begin{array}{l} CH_3 \\ | \\ CH— \\ | \\ CH_2— \end{array} \quad \text{and} \quad \begin{array}{l} CH_2— \\ | \\ CH_2 \\ | \\ CH_2— \end{array}$$

Propylene. Trimethene.

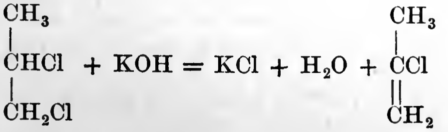
Derivatives of both are known.

478. *Propylene dichloride*, $C_3H_6Cl_2 = CH_3.CHCl.CH_2Cl$, is obtained directly from propylene and chlorine gas, and by the action of chlorine gas upon isopropylic chloride in sunlight :



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

in the latter case obtained together with the metameric methyl chloracetol (§ 445). It is a colourless liquid, boiling at 96°–97°, and has sp. gr. 1·1656 at 14°. By alcoholic potassic hydrate it is converted into monochlor propylene (boiling at 23°) :



$$\begin{array}{l} CH_3 \\ | \\ CHCl \\ | \\ CH_2Cl \end{array} + KOH = KCl + H_2O + \begin{array}{l} CH_3 \\ | \\ CCl \\ || \\ CH_2 \end{array}$$

the same which is formed from acetone by the action of phosphoric chloride. The chlor propylene, $CH_3.CH:CHCl$, isomeric with this, has not yet been observed.

Propylene dibromide, $C_3H_6Br_2 = CH_3.CHBr.CH_2Br$, is formed by the absorption of propylene gas by bromine, and by heating isopropylic bromide with liquid bromine. It is an oil boiling at 142°, having the sp. gr. 1·974. It is converted into monobrom propylene, $CH_3.CBr.CH_2$ (boiling point 57°–58°), by action of alcoholic potassic hydrate, from which, by heating with hydrobromic acid saturated at + 6°, propylene dibromide is regenerated, whilst by employment of more dilute acid, methyl brom-acetol (§ 445), $CH_3.CBr_2.CH_3$, is formed.

Propylene diiodide, $C_3H_6I_2 = CH_3.CHI.CH_2I$, obtained by direct union of iodine and propylene at a temperature of 50°–60°, is a colourless oil of powerful odour, decomposing on distillation.

Propylene chloro-bromide, $CH_3.CHBr.CH_2Cl$, is obtained by heating monobrom propylene with concentrated hydrochloric acid. It boils at 112°–113°, and is reconverted into monobrom propylene by alcoholic potassic hydrate:

$$CH_3.CHBr.CH_2Cl + KOH = KCl + H_2O + CH_3.CBr:CH_2.$$

The isomeric *propylene bromo-chloride*, $CH_3.CHCl.CH_2Br$, is obtained by continued boiling of propylene dibromide with mercuric bromide:

$$2CH_3.CHBr.CH_2Br + HgCl_2 = HgBr_2 + 2CH_3.CHCl.CH_2Br.$$

It boils constantly between 119° and 120°, and yields monochlor propylene on boiling with alcoholic potassic hydrate:

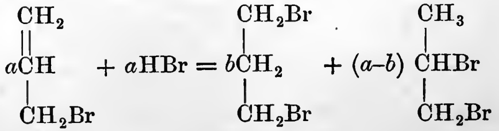
$$CH_3.CHCl.CH_2Br + KOH = KBr + OH_2 + CH_3.CCl:CH_2.$$

On heating propylene haloid compounds with water to 210°–220° in sealed glass tubes, there is obtained, together with halogen hydro-acid, not, as might have been expected, propylene oxide, formed by the direct replacement of the halogen by an atom of oxygen, but the compounds isomeric with this, acetone and propionic aldehyde. Without doubt in these decompositions it is not both hydrogen atoms of the water molecule that are employed to form the halogen hydro-acid, but only one of them, together with a hydrogen atom of the propylene; so that the process proceeds with intermediate phases in the following way:

$$\begin{aligned} CH_3.CHCl.CH_2Cl + HOH &= HCl + CH_3.CCl:CH_2 + HOH \\ &= 2HCl + CH_3.CO.CH_3, \end{aligned}$$

$$\begin{aligned} \text{and } CH_3.CHCl.CH_2.Cl + HOH &= HCl + CH_3.CH:CHCl \\ + HOH &= 2HCl + CH_3.CH_2.CHO. \end{aligned}$$

479. *Trimethene dibromide*, $CH_2Br.CH_2.CH_2Br$, is formed by heating allylic bromide with hydrobromic acid (saturated at 0°) for a short time to 100° in sealed tubes. Some propylene dibromide is always formed also. The process can be expressed by the equation:

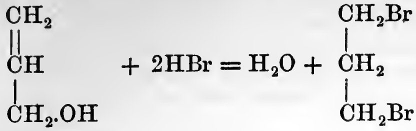


$$\begin{array}{c}CH_2\\ \|\\ aCH\\ |\\ CH_2Br\end{array} + aHBr = \begin{array}{c}CH_2Br\\ |\\ bCH_2\\ |\\ CH_2Br\end{array} + (a-b)\begin{array}{c}CH_3\\ |\\ CHBr\\ |\\ CH_2Br\end{array}$$

Allylic bromide. Trimethene bromide. Propylene bromide.

The isomeric products are separated by fractional distillation.

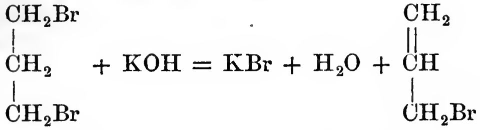
Scarcely anything but trimethene dibromide is obtained when hydrobromic acid is passsed into allyl alcohol at 0°:



$$\begin{array}{l}CH_2\\ \| \\ CH\\ | \\ CH_2.OH\end{array} + 2HBr = H_2O + \begin{array}{l}CH_2Br\\ | \\ CH_2\\ | \\ CH_2Br\end{array}$$

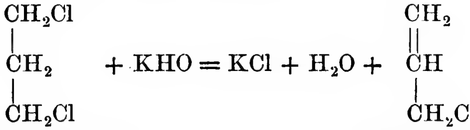
Allylic alcohol.

Trimethene dibromide is a colourless liquid insoluble in water, boiling at 160°–163° (about 20° higher than propylene dibromide) and having sp. gr. 2·0177 at 0°. It is reconverted into allylic bromide by alcoholic potassic hydrate:



$$\begin{array}{l}CH_2Br\\ | \\ CH_2\\ | \\ CH_2Br\end{array} + KOH = KBr + H_2O + \begin{array}{l}CH_2\\ \| \\ CH\\ | \\ CH_2Br\end{array}$$

Trimethene dichloride is obtained, by heating trimethene dibromide for a long time at 160° with mercuric chloride, as a colourless oil boiling at 117°, having at 15° sp. gr. 1·201, and being converted into allylic chloride by alcoholic potassic hydrate:



$$\begin{array}{l}CH_2Cl\\ | \\ CH_2\\ | \\ CH_2Cl\end{array} + KHO = KCl + H_2O + \begin{array}{l}CH_2\\ \| \\ CH\\ | \\ CH_2Cl\end{array}$$

Trimethene dichloride. Allylic chloride.

Higher Homologues.

480. *Butene Dihaloids.*—As yet only few haloid compounds of the three butylenes (§ 476) are known.

Normal butylene dibromide, or *methyl-allyl dibromide:*

$$CH_3.CH_2.CHBr.CH_2Br,$$

boils at 156°–159°, but has probably not yet been obtained quite pure. The bromine compound of the butylene obtained by action of zinc diethyl on monobrom ethylene boils at 166°.

Pseudo-butylene dibromide, $CH_3.CHBr.CHBr.CH_3$, obtained from butylene and bromine, boils at 159°.

Two halogen compounds of *isobutylene* are known. The *dichloride*, $(CH_3)_2:CCl.CH_2Cl$, boils at 130°, the *dibromide* at 149°. Similarly to the propylene dihaloids, which yield propionic aldehyde on boiling with water, isobutylene dibromide gives isobutyric aldehyde:

$$(CH_3):CBr.CH_2Br + H_2O = 2HBr + (CH_3)_2:CH.CHO.$$

481. *Normal amylene dibromide*, or *ethyl-allyl dibromide:*

$$CH_3.CH_2.CH_2.CHBr.CH_2Br,$$

boils at about 175°.

Isoamylene dichloride, $(CH_3)_2.CCl.CHCl.CH_3$, is a colourless distillable oil. *Isoamylene dibromide*, $(CH_3)_2.CBr.CHBr.CH_3$, boils with slight decomposition between 170° and 175°, and yields with alcoholic potassic hydrate *monobrom amylene*, $(CH_3)_2:CH.CBr:CH_3$, whose boiling point is 112°.

482. The dibromides of the higher members of the series, such as hexylene, octylene, and diamylene, are oily liquids which decompose on distillation. Some of these bodies will be mentioned later.

The Diacid Alcohols or Glycols, $C_nH_{2n}(OH)_2$.

483. The methods used for preparing the glycols or dihydrates of the divalent alcohol radicals vary with the nature of these bodies. In most cases the dihaloid compounds are employed, and are first converted into the acetates.

A good yield is obtained by employing the diiodides or dibromides of the olefines, and heating them with argentic acetate in presence of glacial acetic acid:

$$C_nH_{2n}I_2 + 2AgO.C_2H_3O = 2AgI + C_nH_{2n}(O.C_2H_3O)_2.$$

The diacetate is first purified by distillation, and then saponified by addition of just the requisite quantity of alkali:

$$C_nH_{2n}(O.C_2H_3O)_2 + 2KOH = 2KO.C_2H_3O + C_nH_{2n}(OH)_2.$$

Another, if also analogous, way consists in heating the dibromides or dichlorides of the olefines with alcohol and potassic acetate to 100°, until the reaction is complete. There is then formed potassic and ethylic acetates together with the olefine hydrate acetate:

$$C_nH_{2n}Br_2 + HOC_2H_5 + 2KO.C_2H_3O = 2KBr + C_2H_5O.C_2H_3O \\ + C_nH_{2n}(OH)(O.C_2H_3O),$$

which is also purified by rectification and then decomposed by the requisite quantity of strong basic hydrate, and the glycol separated by fractional distillation.

The double tertiary glycols or pinacones are prepared from the ketones by action of nascent hydrogen.

484. The glycols are mostly syrupy liquids, the lower members mixing in all proportions with water, but, like the alcohols, $C_nH_{2n+1}.OH$, becoming less soluble with rise in molecular weight. They are soluble in alcohol without exception, mostly also in ether. So far as the members of this series have yet been obtained, they distil unaltered and generally taste sweet.

By action of hydrochloric acid gas they are converted into monohydrate chlorides:

$$C_nH_{2n}(OH)_2 + HCl = C_nH_{2n}\begin{cases}Cl \\ OH\end{cases}$$

which by action of phosphoric chloride are converted into the dichlorides:

$$C_nH_{2n}\begin{cases}Cl \\ OH\end{cases} + PCl_5 = POCl_3 + HCl + C_nH_{2n}Cl_2.$$

Hydrobromic, and especially hydriodic, acids convert the glycols with greater readiness and completely into the respective dihaloids.

By heating with concentrated hydriodic acid to 150°–200° alkyl iodides are formed:

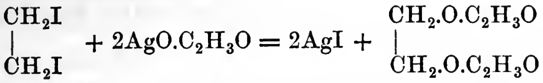
$$C_nH_{2n}(OH)_2 + 3HI = 2OH_2 + I_2 + C_nH_{2n+1}I,$$

and even paraffins:

$$C_nH_{2n}(OH)_2 + 4HI = 2H_2O + 2I_2 + C_nH_{2n+2}.$$

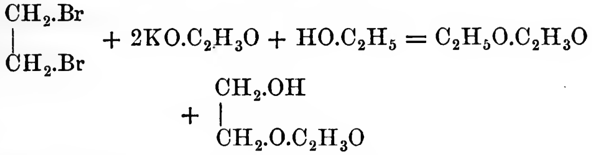
Ethylene Glycol, $C_2H_6O_2 = C_2H_4(OH)_2$.

485. To obtain ethylene dihydrate or ethylene glycol, frequently also termed glycol, either ethylene diacetate, boiling at 187°, is prepared by heating ethylene diiodide with argentic acetate in presence of glacial acetic acid at 100°:



$$\begin{array}{l}CH_2I\\ |\\ CH_2I\end{array} + 2AgO.C_2H_3O = 2AgI + \begin{array}{l}CH_2.O.C_2H_3O\\ |\\ CH_2.O.C_2H_3O\end{array}$$

or ethylene hydrate acetate (boiling at 182°) is prepared from ethylene dichloride or dibromide, alcohol, and potassic acetate:



$$\begin{array}{l}CH_2.Br\\ |\\ CH_2.Br\end{array} + 2KO.C_2H_3O + HO.C_2H_5 = C_2H_5O.C_2H_3O + \begin{array}{l}CH_2.OH\\ |\\ CH_2.O.C_2H_3O\end{array}$$

In employing this latter, generally preferable, method, equal parts of potassic acetate and ethylene dibromide are placed in a thick-walled flask—e.g. champagne bottles—two parts of alcohol are then added, and, after securing the cork in its place, are heated for several hours on the water bath. If ethylene chloride be employed, the proportions must be altered to one part of this, two parts of potassic acetate, and four parts of alcohol.

After cooling the heated mixture much potassic chloride or bromide is found to have crystallised out; the alcoholic solution is filtered, the alcohol and ethylic acetate distilled off, and that portion passing over at higher temperatures submitted to fractional distillation. To that passing over between 140° and 200°, mostly ethylene hydrate acetate, a hot concentrated solution of potassic hydrate is slowly added, until a distinctly alkaline reaction is obtained after long shaking. Carbonic anhydride is then passed in to convert the free alkali into carbonate, and the whole submitted to distillation. Water first passes over. Ethylene glycol is obtained by repeated fractionation from that portion distilling above 100°.

Instead of potassic hydrate, the saponification may be effected in similar manner by hot saturated solution of baric hydrate. After precipitation of the excess of baric hydrate by carbonic anhydride, the whole is evaporated as far as possible on the water bath, the baric acetate precipitated from the residue by addition of absolute alcohol, and the glycol separated from the alcoholic filtrate by fractional distillation.

Ethylene glycol can be obtained in one operation from ethylene dibromide, when molecular weights of it and of potassic acetate are heated with double the weight of alcohol in a vessel provided with an inverted condenser, and the filtered liquid submitted to fractional distillation. About one-half of the bromide is obtained unchanged, the other half in great part as ethylene glycol. Undoubtedly ethylene bromide acetate is first formed :

$$2C_2H_4Br_2 + 2KO.C_2H_3O = 2KBr + 2C_2H_4Br(O.C_2H_3O),$$

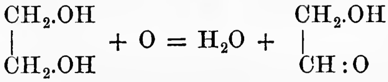
which is resolved by the alcohol present into ethylic acetate, ethylene dibromide, and glycol :

$$2C_2H_4Br(OC_2H_3O) + 2C_2H_5.OH = C_2H_4Br_2 + 2C_2H_5.O.C_2H_3O + C_2H_4(OH)_2.$$

486. Ethylene glycol is a colourless liquid, of about the consistence of a thin syrup, of sweet and alcoholic taste, and scarcely any smell. Its sp. gr. is 1·125 at 0°, the vapour density 2·164. Its boiling point is 197°.

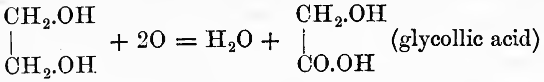
It mixes with water and alcohol in every proportion, but is less soluble in ether. Sodium dissolves in it, with evolution of hydrogen, the compound, $C_2H_4\left\{\begin{array}{l}OH\\ONa\end{array}\right.$, corresponding to sodic ethylate, being first formed as a solid white mass. By heating to 190° with as much sodium again, this is converted, though completely only with difficulty, into *disodic ethylenate*, $C_2H_4(ONa)_2$. Like the sodium derivatives of the C_nH_{2n+1} alcohols, both these bodies are decomposed by water, yielding glycol and sodic hydrate.

487. Ethylene glycol, as a diprimary alcohol, is capable of similar oxidation to the primary monacid alcohols; only this can be repeated twice. The first stage of oxidation that might have been expected :



$$\begin{array}{c}CH_2.OH\\|\\CH_2.OH\end{array} + O = H_2O + \begin{array}{c}CH_2.OH\\|\\CH:O\end{array}$$

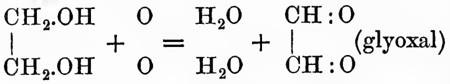
has not yet been realised, the oxidation always proceeding beyond this point. If two oxygen atoms act on a molecule of glycol, *glycollic acid* is formed :



$$\begin{array}{c}CH_2.OH\\|\\CH_2.OH\end{array} + 2O = H_2O + \begin{array}{c}CH_2.OH\\|\\CO.OH\end{array} \quad \text{(glycollic acid)}$$

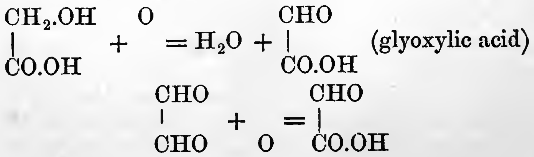
which is related to glycol as acetic acid is to ethyl alcohol.

By the same proportion of the ingredients the double aldehyde *glyoxal* is also readily formed :



$$\begin{array}{c}CH_2.OH\\|\\CH_2.OH\end{array} + \begin{array}{c}O\\ \\O\end{array} = \begin{array}{c}H_2O\\ \\H_2O\end{array} + \begin{array}{c}CH:O\\|\\CH:O\end{array} \quad \text{(glyoxal)}$$

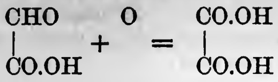
Both oxidation products are converted by further oxidation into an aldehydic acid, *glyoxylic acid :*



$$\begin{array}{c}CH_2.OH\\|\\CO.OH\end{array} + \begin{array}{c}O\\ \\ \\\end{array} = H_2O + \begin{array}{c}CHO\\|\\CO.OH\end{array} \quad \text{(glyoxylic acid)}$$

$$\begin{array}{c}CHO\\|\\CHO\end{array} + \begin{array}{c}\\ \\O\end{array} = \begin{array}{c}CHO\\|\\CO.OH\end{array}$$

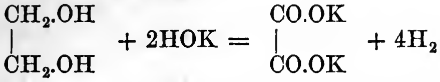
which finally yields the dibasic *oxalic acid* :



$$\begin{array}{l}\mathrm{CHO}\\ |\\ \mathrm{CO.OH}\end{array} + \mathrm{O} = \begin{array}{l}\mathrm{CO.OH}\\ |\\ \mathrm{CO.OH}\end{array}$$

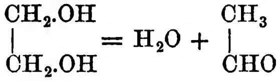
Both the primary alcohol groups $CH_2.OH$, united in glycol, therefore suffer the same changes as in the primary monacid alcohols (§ 384).

By heating with potassic hydrate, ethylene alcohol yields an oxalate, hydrogen being evolved :



$$\begin{array}{l}\mathrm{CH_2.OH}\\ |\\ \mathrm{CH_2.OH}\end{array} + 2\mathrm{HOK} = \begin{array}{l}\mathrm{CO.OK}\\ |\\ \mathrm{CO.OK}\end{array} + 4\mathrm{H_2}$$

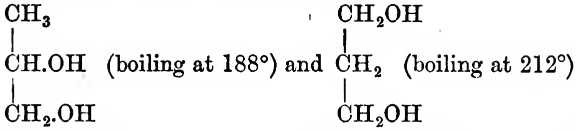
Zincic chloride, on gentle heating, converts it, with elimination of water, into acetic aldehyde :



$$\begin{array}{l}\mathrm{CH_2.OH}\\ |\\ \mathrm{CH_2.OH}\end{array} = \mathrm{H_2O} + \begin{array}{l}\mathrm{CH_3}\\ |\\ \mathrm{CHO}\end{array}$$

Tricarbon Glycols, $C_3H_6(OH)_2$.

488. The two possible isomeric tricarbon glycols :



$$\begin{array}{l}\mathrm{CH_3}\\ |\\ \mathrm{CH.OH}\\ |\\ \mathrm{CH_2.OH}\end{array} \text{(boiling at 188°) and } \begin{array}{l}\mathrm{CH_2OH}\\ |\\ \mathrm{CH_2}\\ |\\ \mathrm{CH_2OH}\end{array} \text{(boiling at 212°)}$$

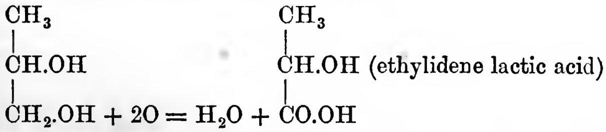
Propylene glycol,
α-oxypropylic alcohol.

Trimethene glycol,
β-oxypropylic alcohol.

are known.

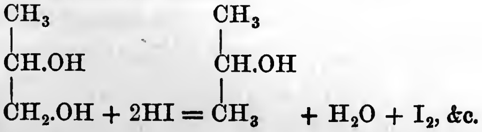
1. Propylene glycol, or α-oxypropylic alcohol, is prepared from propylene dibromide. By decomposition with argentic acetate the diacetate, boiling at 186°, is first obtained, and from this, on saponification, the alcohol. This latter is colourless, syrupy, and of sweet taste; its sp. gr. at 0° is 1·051, its boiling point 188°, and the vapour density 2·596.

By oxidation of propylene glycol diluted with water, by means of platinum black and oxygen, it behaves as though only a monhydric primary alcohol yielding an acid of like carbon contents—ethylidene lactic acid, which is at the same time a secondary alcohol :



$$\begin{array}{l}\mathrm{CH_3}\\ |\\ \mathrm{CH.OH}\\ |\\ \mathrm{CH_2.OH}\end{array} + 2\mathrm{O} = \mathrm{H_2O} + \begin{array}{l}\mathrm{CH_3}\\ |\\ \mathrm{CH.OH}\\ |\\ \mathrm{CO.OH}\end{array} \text{(ethylidene lactic acid)}$$

By heating with hydriodic acid to 100° isopropylic alcohol and isopropylic iodide are formed :

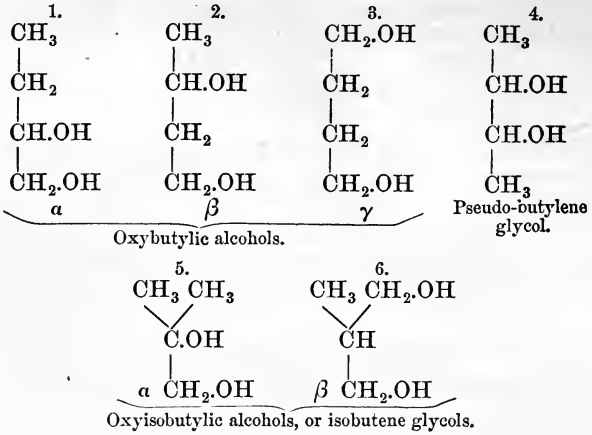


$$\begin{array}{l}\mathrm{CH_3}\\ |\\ \mathrm{CH.OH}\\ |\\ \mathrm{CH_2.OH}\end{array} + 2\mathrm{HI} = \begin{array}{l}\mathrm{CH_3}\\ |\\ \mathrm{CH.OH}\\ |\\ \mathrm{CH_3}\end{array} + \mathrm{H_2O} + \mathrm{I_2}, \text{&c.}$$

2. *Trimethene glycol*, a double primary alcohol, is obtained in the manner already described, first as diacetate (boiling point 203°–205°), and further, on saponification of this, as a syrupy, sweet-tasting liquid boiling at 212°.

Tetracarbon Glycols, $C_4H_8(OH)_2$.

489. Of the six possible isomers of this formula:



only three have yet been obtained. They are

1. *a-Butene glycol*, $CH_3.CH_2.CH(OH).CH_2.OH$, is obtained from the dibromide of normal butylene. It is a syrupy liquid boiling at 192°, of sp. gr. 1·0189, and on oxidation yields glycollic and glyoxylic acids.

2. *β-Butene glycol*, or *β-oxybutylic alcohol*:

$$CH_3.CH(OH).CH_2.CH_2.OH.$$

This compound is obtained, together with ethylic alcohol, by the action of sodium amalgam upon acetic aldehyde. The aldehyde for this purpose is distilled with three to six times its volume of water, and one per cent. sodium amalgam slowly added, the liquid being kept nearly acid by addition of hydrochloric acid in small quantities. The liquid at the close of the reaction is poured off from the mercury, neutralised with sodic hydrate, and everything volatile below 100° distilled off, the residue shaken with ether to remove other products, and the aqueous layer evaporated as far as possible on the water bath. Strong alcohol is then added to precipitate sodic chloride, and the filtered liquid submitted to distillation. β-Butene glycol passes over at 203·5°–204°. It is a colourless, sweet-tasting, viscid liquid, which mixes with water and alcohol, but is not perceptibly soluble in ether.

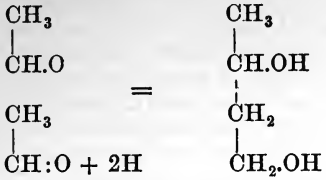
Nitric acid and chromic acid oxidise it to acetic acid, oxalic acid, carbonic anhydride, crotonic aldehyde, with some acetic aldehyde:

$$CH_3.CH(OH).CH_2.CH_2.OH + 6O = \underset{\text{Acetic acid.}}{CH_3.CO.OH}$$

$$+ \underset{\text{Oxalic acid.}}{HO.CO.CO.OH} + 2H_2O.$$

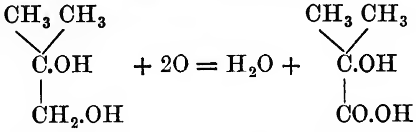
$$\mathrm{CH_3.CH(OH).CH_2.CH_2.OH + 6O = CH_3.CHO + 2CO_2 + 3H_2O.}$$
$$\mathrm{CH_3.CH(OH).CH_2.CH_2.OH + O = CH_3.CH{:}CH.CHO + 2H_2O.}$$

In the formation of β-butene glycol two aldehyde molecules coalesce under the action of nascent hydrogen :



$$\begin{array}{l} \mathrm{CH_3} \\ | \\ \mathrm{CH.O} \\ \\ \mathrm{CH_3} \\ | \\ \mathrm{CH{:}O + 2H} \end{array} = \begin{array}{l} \mathrm{CH_3} \\ | \\ \mathrm{CH.OH} \\ | \\ \mathrm{CH_2} \\ | \\ \mathrm{CH_2.OH} \end{array}$$

3. *α-Isobutene glycol,* termed *isobutylene glycol,* is usually prepared from isobutylene dibromide. It resembles the preceding, boils between 183° and 184°, and has at 0° the sp. gr. 1·048. It is converted into α-oxyisobutyric acid by dilute nitric acid :

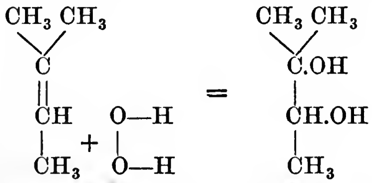


490. Only three of the numerous possible isomeric pentene glycols are known, namely :

α-Pseudo-amylene glycol, $\mathrm{CH_3.CH_2.CH(OH).CH(OH).CH_3}$, prepared from the dibromide of ethyl-methyl methene, boils at 188° and has sp. gr. ·9945.

α-Isoamylene glycol, $\mathrm{(CH_3)_2CH.CH(OH).CH_2OH}$, obtained from the dibromide of the isoamylene (§ 467, 4), is a thick liquid, boiling at 206° and of sp. gr. ·9987.

β-Isoamylene glycol, $\mathrm{(CH_3)_2{:}C(OH)CH(OH).CH_3}$, obtained from isoamylene dibromide in the way already frequently mentioned, and also by the direct combination of isoamylene with hydric peroxide :



It is a bitter-tasting, syrupy liquid, which boils at 177° and has at 0° the sp. gr. ·987. It dissolves in water, alcohol, and ether, and on oxidation yields oxyisobutyric acid, $\mathrm{(CH_3)_2.C(OH).CO.OH}$.

Hexene Glycols, $\mathrm{C_6H_{12}.(OH)_2}$.

491. 1. A *hexylene glycol* is obtained from the dibromide of the hexylene mentioned in § 468 as obtained from α-normal secondary hexylic iodide. It is a thick liquid, miscible with water, of ·967 sp. gr. and 207° boiling point.

2. *Diallyl dihydrate* is probably a double secondary normal

hexene glycol of the formula $CH_3.CH(OH).CH_2.CH_2.CH(OH).CH_3$. To prepare it diallyl is heated for several hours with concentrated hydriodic acid, whereby it unites with two molecules of HI, and is converted into *diallyl dihydroiodide*, $C_6H_{12}I_2$:

$$CH_2{:}CH.CH_2.CH_2.CH{:}CH_2 + 2HI = CH_3.CHI.CH_2.CH_2.CHI.CH_3.$$

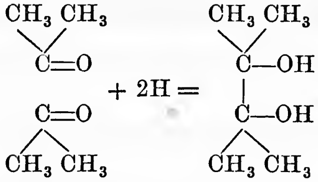
This reacts with argentic acetate even in the cold, forming the corresponding diacetate, which boils at 225°–230°, and on saponification with alkali yields *diallyl dihydrate* as a colourless thick syrup, which has at 0° sp. gr. ·9638, boils between 212° and 215°, and mixes with water, alcohol, and ether. By heating with concentrated hydrochloric acid it yields its dichloride, the so-called *diallyl dihydrochloride*:

$$CH_3.CHCl.CH_2.CH_2.CHCl.CH_3,$$

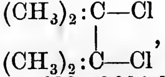
which is also obtained by the direct union of diallyl with hydrochloric acid as an oil boiling between 170° and 180°.

On oxidation diallyl dihydrate yields only acetic and carbonic acids.

3. *Pinacone*, $(CH_3)_2{:}C(OH).C(OH){:}(CH_3)_2$, is the double tertiary alcohol of the formula $C_6H_{12}(OH)_2$. It is obtained, together with isopropylic alcohol, by the action of nascent hydrogen upon acetone, and is formed especially when the acetone is employed in considerable excess:



To prepare this body acetone is poured upon a large quantity of a half saturated solution of potassic carbonate, and sodium added in pieces about the size of a pea. These sink through the layer of acetone, and on reaching the aqueous solution evolve hydrogen, which is completely fixed by the acetone. One part of sodium is employed to about three parts of acetone. When the reaction is completed the upper layer is submitted to distillation, and about one and a half per cent. of crude isopropylic alcohol is obtained below 100°. At higher temperatures pinacone passes over, and is obtained on cooling as a crystalline mass. To purify it, it is dissolved in water and evaporated, when it separates in large quadratic tables, $C_6H_{12}(OH)_2,6H_2O$, melting at 42°, and which lose their water of crystallisation slowly in dry air. On distillation water first passes over, and later, at about 170°, anhydrous pinacone. This latter is a colourless crystalline mass, which melts at 38° and boils between 171° and 172°. By phosphoric oxychloride pinacone is converted into the corresponding dichloride,



$$\begin{array}{l}(CH_3)_2{:}C{-}Cl\\ \qquad\;|\\ (CH_3)_2{:}C{-}Cl\end{array}$$

, a crystalline mass melting at 160°.

492. Of higher molecular glycols only *octylene glycol*, prepared from the dibromide of caprylene (§ 469), is sufficiently known to be worth mention. It is a colourless liquid miscible with alcohol and ether, *insoluble in water*, of ·932 sp. gr., and boiling at 235°–240°.

Haloid Hydrates of the Glycol Radicals.

493. On passing hydrochloric gas into an olefine glycol, one of the hydrogen groups is first replaced by chlorine:

$$C_nH_{2n}(OH)_2 + HCl = C_nH_{2n}\left\{\begin{matrix}Cl\\OH\end{matrix}\right. + H_2O.$$

The corresponding replacement of the second hydroxyl group occurs with far greater difficulty, but, as previously mentioned (§ 484), can be effected by phosphoric chloride. Hydriodic acids react more vigorously, forming the diiodide from the glycol.

Other methods of preparing the hydrate haloids depend on the direct union of the halogen hydro-acids to the acids of the glycol radicals, and on the power of the olefines of uniting directly with hypochlorous acid:

$$C_nH_{2n} + ClOH = C_nH_{2n}(OH)Cl.$$

494. By action of alkaline solutions the haloid hydrates are not reconverted into glycols, but into the anhydrous oxides of the glycol radicals:

$$C_nH_{2n}\left\{\begin{matrix}Cl\\OH\end{matrix}\right. + KOH = KCl + H_2O + C_nH_{2n}{:}O.$$

These anhydrous oxides unite very readily with halogen hydro-acids and are thereby reconverted into haloid hydrates:

$$C_nH_{2n}{:}O + HBr = C_nH_{2n}\left\{\begin{matrix}Br\\OH\end{matrix}\right.$$

To obtain the glycols from these latter, they must first be converted into hydrate acetates by heating with potassic acetate:

$$C_nH_{2n}\left\{\begin{matrix}Cl\\OH\end{matrix}\right. + KO.C_2H_3O = KCl + C_nH_{2n}\left\{\begin{matrix}O.C_2H_3O\\OH\end{matrix}\right.$$

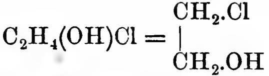
and afterwards saponified.

By treatment with sodium amalgam and water the hydrate haloids yield the monovalent alcohols:

$$C_nH_{2n}Cl.OH + Na_2 + H_2O = NaCl + NaOH + C_nH_{2n+1}.OH.$$

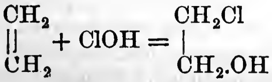
495. The *ethylene hydrate haloids* are the best known.

1. *Ethylene hydrate chloride*, or *glycol chlorhydrin:*



$$C_2H_4(OH)Cl = \begin{matrix}CH_2.Cl\\|\\CH_2.OH\end{matrix}$$

is formed by passing hydrochloric acid gas into ethylene glycol and distillation of the mixture after standing some days. The compound can also be prepared from ethylene and an aqueous solution of hypochlorous acid:

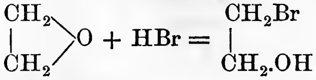


$$\begin{matrix}CH_2\\\|\\CH_2\end{matrix} + ClOH = \begin{matrix}CH_2Cl\\|\\CH_2.OH\end{matrix}$$

In employing the latter method chlorine gas is passed into ice-cold water in which yellow mercuric oxide is suspended, and the solution of hypochlorous acid so prepared poured into a balloon filled with ethylene, and allowed to remain for some days in the dark. The acid liquid is then neutralised with sodic hydrate and submitted to distillation, as long as the liquid passing over still tastes sweet. Ethylene chloro-hydrate is then removed from the distillate by shaking with ether, and after evaporation of the ether purified by fractional distillation.

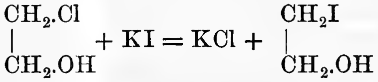
It is a colourless liquid of somewhat sweet taste, boiling at 128°, and completely miscible with water.

2. *Ethylene hydrate bromide*, $CH_2Br.CH_2.OH$, can be prepared from ethylene oxide and hydrobromic acid; it boils at 147° :



$$\left.\begin{array}{l}CH_2\\|\\CH_2\end{array}\right\rangle O + HBr = \begin{array}{l}CH_2Br\\|\\CH_2.OH\end{array}$$

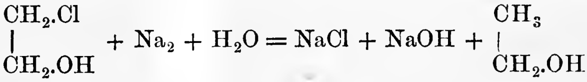
3. *Ethylene hydrate iodide* is obtained by heating the chloride with potassic iodide :



$$\begin{array}{l}CH_2.Cl\\|\\CH_2.OH\end{array} + KI = KCl + \begin{array}{l}CH_2I\\|\\CH_2.OH\end{array}$$

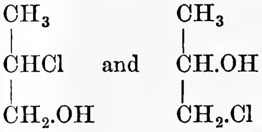
as a heavy liquid, which cannot be distilled unchanged.

By action of sodium amalgam the acidulated aqueous solutions of all three hydrate haloids yield ethylic alcohol :



$$\begin{array}{l}CH_2.Cl\\|\\CH_2.OH\end{array} + Na_2 + H_2O = NaCl + NaOH + \begin{array}{l}CH_3\\|\\CH_2.OH\end{array}$$

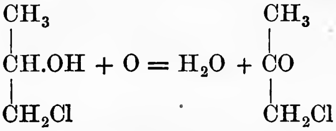
496. Propylene glycol can yield with hydro-acids two isomeric hydrate haloids :



$$\begin{array}{l}CH_3\\|\\CHCl\\|\\CH_2.OH\end{array} \quad \text{and} \quad \begin{array}{l}CH_3\\|\\CH.OH\\|\\CH_2.Cl\end{array}$$

but only compounds of the latter variety are known with certainty.

Propylene hydrate chloride, or *propylene chlorhydrin*, obtained from propylene glycol and hydrochloric acid, or from propylene gas and hypochlorous acid, is a colourless liquid, boiling at 127°, which on careful oxidation yields monochlor acetone :



$$\begin{array}{l}CH_3\\|\\CH.OH\\|\\CH_2Cl\end{array} + O = H_2O + \begin{array}{l}CH_3\\|\\CO\\|\\CH_2Cl\end{array}$$

Propylene oxide combines with hydrobromic acid, forming *propylene hydrate bromide*, which boils between 145° and 148°, and yields with hydriodic acid *propylene hydrate iodide*. This latter compound is decomposed on distillation at ordinary atmospheric pressure, but distils unaltered at a pressure of 60 mm. at 105°.

β-Isoamylene hydrate chloride, $C_5H_{10}\left\{\begin{array}{l}Cl\\OH\end{array}\right.$, can be obtained from isoamylene glycol and hydrochloric acid, or by union of isoamylene and hypochlorous acid. It possesses a strong odour, recalling that of valeric acid, is soluble in water, and boils at 155°.

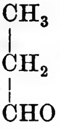
Octylene hydrate chloride, $C_8H_{16}\left\{\begin{matrix}Cl\\OH\end{matrix}\right.$, obtained from caprylene and hypochlorous acid, is a yellowish viscous liquid of camphor-like odour, decomposing on boiling. It has sp. gr. 1·003 at 0°.

Ethereal Derivatives of the Glycols.

497. In addition to the anhydrous oxides of the glycol derivatives and their polymers, the so-called poly-ethylenic alcohols and the ethylene ethyl oxides must be classified amongst the ethereal glycol derivatives.

Anhydrous Oxides of the Glycol Radicals, $C_nH_{2n}O$, *and their Polymers.*

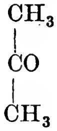
498. The anhydrous oxides of the olefines are formed, as already mentioned (§ 494), by the decomposition of the haloid hydrates by alkalies. They are isomeric with the aldehydes and ketones of like carbon contents, but are distinguished from both groups of compounds by the oxygen being united to two different—without exception neighbouring—carbon atoms of the chain:



$$\begin{matrix}CH_3\\|\\CH_2\\|\\CHO\end{matrix}$$

(boils at 49·5°)

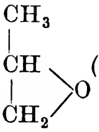
Propylic aldehyde.



$$\begin{matrix}CH_3\\|\\CO\\|\\CH_3\end{matrix}$$

(boils at 58°)

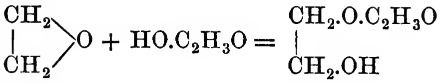
Acetone.



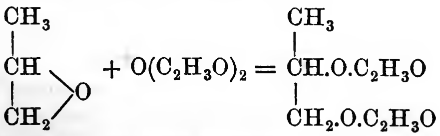
(boils at 35°)

So far as known, these bodies possess much lower boiling points than the isomeric members of the other two groups.

499. That these bodies unite with the halogen hydro-acids to form hydrate haloids has been already mentioned. In a similar way they unite with the oxyacids to form basic salts:

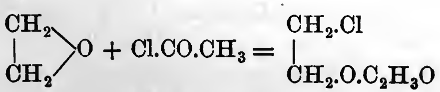


With acid anhydrides they yield neutral salts:



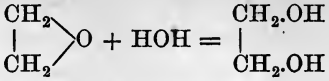
Acetic anhydride.

and with the acid chlorides they give compounds analogous to the hydrate chlorides:

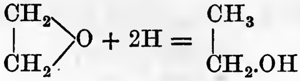


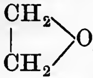
Acetic chloride.

They also unite with water, especially on heating, and are thereby converted directly into glycols:



By nascent hydrogen the olefine oxides are converted into the monhydric alcohols:



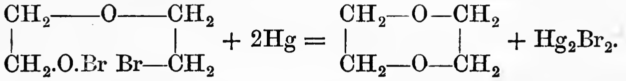
500. *Ethylene oxide*, C_2H_4O =  isomeric with acetic aldehyde, is obtained by mixing ethylene hydrate chloride with potassic hydrate, and condensing the vapours, previously dried by quick-lime, in strongly cooled receivers.

It is a colourless, mobile, agreeably smelling liquid, boiling at 13·5°, of sp. gr. ·898 at 0°, and having a vapour density of 1·432. It mixes in every proportion with water, and unites slowly with it, forming ethylene glycol. It is converted into ethylic alcohol by action of nascent hydrogen.

Ethylene oxide not only unites with free acids, but also decomposes the salts of weak basic metals with strong acids. It precipitates, for instance, the hydrates of magnesium, aluminium, and iron from the respective salts:

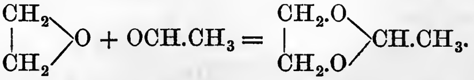
$$Mg\left\{\begin{matrix}O.SO_2.OH\\OH\end{matrix}\right. + C_2H_4{:}O + H_2O = Mg(OH)_2$$
$$+ C_2H_4\left\{\begin{matrix}O.SO_2.OH\\OH\end{matrix}\right.$$

501. On slowly mixing well-cooled ethylene oxide with bromine, there is obtained a compound forming yellowish red crystals of the formula $(C_2H_4O)_2Br_2$. These melt at 65°, boil at 95°, and are obtained again unaltered on condensation of the vapours. Metallic mercury withdraws the bromine, and gives diethylene dioxide:



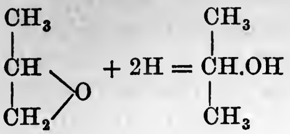
This is, in the cold, a white crystalline mass, soluble in water, alcohol, and ether; it melts at 9°, and at 0° has sp. gr. 1·048. The boiling point is 102°, the vapour density 3·1.

Isomeric with diethylene dioxide, and corresponding to acetal (§ 402), is *ethylene ethylidene oxide*, which is obtained, by heating ethylene oxide with acetic aldehyde in sealed glass tubes, as a colourless liquid, boiling at 82·5°:



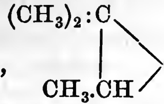
It has at 0° sp. gr. 1, dissolves in one and a half times its weight of water, but is again separated on adding potassic hydrate.

502. *Propylene oxide* boils at 35°, mixes with water, and is converted into isopropylic alcohol by action of nascent hydrogen :



$$\left.\begin{array}{l}CH_3\\ |\\ CH\\ |\\ CH_2\end{array}\right>O + 2H = \begin{array}{l}CH_3\\ |\\ CH.OH\\ |\\ CH_3\end{array}$$

It has sp. gr. ·859 at 0°.

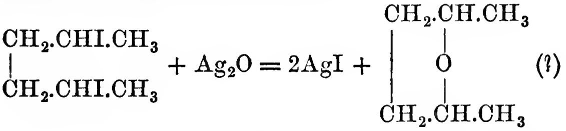


503. *Isoamylene oxide,* $\left.\begin{array}{l}(CH_3)_2:C\\ \quad |\\ CH_3.CH\end{array}\right>O$, prepared from isoamylene hydrate chloride, is a liquid insoluble in water, of sp. gr. ·824 at 0° and boiling at 95°.

504. Two oxides are known corresponding to two of the hexene glycols (§ 491).

1. *Hexylene oxide,* $C_6H_{12}O$, is obtained from hexylene glycol by saturating with hydrochloric acid and decomposing the product with potassic hydrate.

2. *Diallyl hydrate* is formed amongst other products by the action of argentic oxide on diallyl dihydro-iodide :



$$\begin{array}{l}CH_2.CHI.CH_3\\ |\\ CH_2.CHI.CH_3\end{array} + Ag_2O = 2AgI + \begin{array}{|ll}CH_2.CH.CH_3\\ \quad\quad |\\ \quad\quad O\\ \quad\quad |\\ CH_2.CH.CH_3\end{array} \quad (?)$$

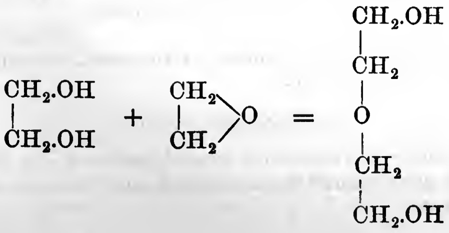
It is a colourless liquid of penetrant aromatic odour, which boils between 93° and 95°, has sp. gr. ·8367 at 0° and vapour density 3·6. It is reconverted into diallylic dihydro-iodide by action of hydriodic acid.

505. *Octylene oxide,* $C_8H_{16}O$, is an oil boiling at 145°.

Poly-ethylenic Alcohols.

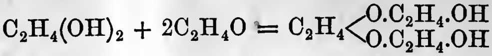
506. In similar manner to its reaction with water ethylene oxide unites with ethylene glycol, especially when heated in sealed tubes at 100°, and thereby yields the *poly-ethylenic glycols,* in which several ethylene groups are united together by oxygen, and two of them also united to hydroxyl. From the mixed product of the reaction there can be isolated on fractional distillation

Diethylene alcohol, or *diethylene oxy-dihydrate,* $O<\begin{array}{l}C_2H_4.OH\\ C_2H_4.OH\end{array}$, as a thick liquid boiling at 250°. It is formed according to the equation :



$$\begin{array}{l}CH_2.OH\\ |\\ CH_2.OH\end{array} + \left.\begin{array}{l}CH_2\\ |\\ CH_2\end{array}\right>O = \begin{array}{l}CH_2.OH\\ |\\ CH_2\\ |\\ O\\ |\\ CH_2\\ |\\ CH_2.OH\end{array}$$

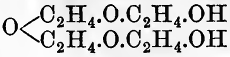
Triethylene alcohol, or *triethylene dioxy-dihydrate*, is formed from two molecules of ethylene oxide and one molecule of glycol:



$$C_2H_4(OH)_2 + 2C_2H_4O = C_2H_4\left<\begin{array}{l}O.C_2H_4.OH\\O.C_2H_4.OH\end{array}\right.$$

and boils at 285°–289°.

Tetrethylene alcohol, or *tetrethylene trioxy-dihydrate:*



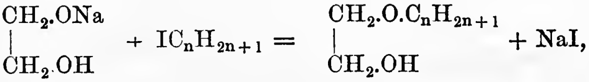
$$O\left<\begin{array}{l}C_2H_4.O.C_2H_4.OH\\C_2H_4.O.C_2H_4.OH\end{array}\right.$$

boils above 300°.

By distillation under reduced pressure (35 mm.) a *hexethylene alcohol*, $(C_2H_4)_6O_5(OH)_2$, can be separated from the less volatile portion. On heating these poly-ethylenic alcohols with acetic acid, both hydroxylic hydrogens are replaced by the acid radical, with formation of diacetates.

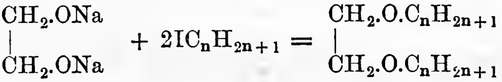
Ethylene Ethyl Ethers.

507. If the sodium derivatives of ethylene glycol (§ 486) be treated with alkyl iodides, the alkyl derivatives of ethylene glycol are formed in addition to sodic iodide:



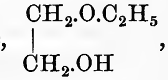
$$\begin{array}{l}CH_2.ONa\\|\\CH_2.OH\end{array} + IC_nH_{2n+1} = \begin{array}{l}CH_2.O.C_nH_{2n+1}\\|\\CH_2.OH\end{array} + NaI,$$

and

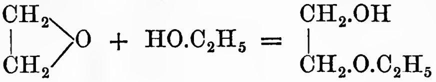


$$\begin{array}{l}CH_2.ONa\\|\\CH_2.ONa\end{array} + 2IC_nH_{2n+1} = \begin{array}{l}CH_2.O.C_nH_{2n+1}\\|\\CH_2.O.C_nH_{2n+1}\end{array}$$

The ethylene ethyl ethers are obtained in this way.

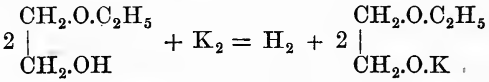


Monethyl glycol ether, or *ethylene hydrate ethylate*, $\begin{array}{l}CH_2.O.C_2H_5\\|\\CH_2.OH\end{array}$, is an agreeable-smelling liquid, boiling at 127°. It is also formed by the direct combination of ethylene oxide and ethylic alcohol:



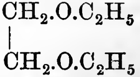
$$\left.\begin{array}{l}CH_2\\|\\CH_2\end{array}\right>O + HO.C_2H_5 = \begin{array}{l}CH_2.OH\\|\\CH_2.O.C_2H_5\end{array}$$

Potassium dissolves therein with evolution of hydrogen:



$$2\begin{array}{l}CH_2.O.C_2H_5\\|\\CH_2.OH\end{array} + K_2 = H_2 + 2\begin{array}{l}CH_2.O.C_2H_5\\|\\CH_2.O.K\end{array}$$

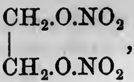
The resulting solid mass yields, by heating with ethylic iodide,



Diethyl glycollic ether, or *ethylene diethylate*, $\begin{array}{l}CH_2.O.C_2H_5\\|\\CH_2.O.C_2H_5\end{array}$, a mobile liquid boiling at 123·5°, isomeric with acetal or ethylidene diethylate (boiling at 105°, § 405).

Glycollic Salts.

508. Besides the basic and normal acetates but few acid derivatives of the glycols have been prepared, and these in general only of ethylene glycol.



Ethylene dinitrate, $\begin{array}{l}CH_2.O.NO_2\\ |\\ CH_2.O.NO_2\end{array}$, is easily obtained by pouring one part of ethylene glycol into an ice-cold mixture of two and a half parts of concentrated nitric acid and five parts of sulphuric acid. Addition of water precipitates the nitrate as a heavy oil of unpleasant sweet taste; this is then washed with sodic hydrate and dried by calcic chloride. On heating it burns with strong detonation and luminous flame. Potassic hydrate readily saponifies it, yielding glycol and potassic nitrate.

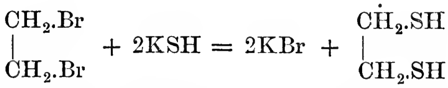
Ethylene hydrate sulphate, $HO.CH_2.CH_2.O.SO_2.OH$, is formed, similarly to the monalkyl sulphates, on gentle heating of ethylene glycol and concentrated sulphuric acid. The product is diluted with water, saturated with baric carbonate, and the filtered solution evaporated to crystallisation. The salt, $(HO.CH_2.CH_2.O.SO_2.O)_2Ba$, so obtained gives, on boiling with baric hydrate, a precipitate of baric sulphate, ethylene glycol remaining in solution.

Sulphur Compounds of Ethylene.

509. *Mercaptans.*—As a diad radical ethylene can unite with two or also with only one SH group, though self-evidently in the last case saturation must be completed by other elements.

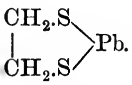
These bodies can be prepared, similarly to the mercaptans of the alkyls (§ 237), by heating the respective haloids with potassic sulphhydrate. The hydrogen atom in union with sulphur is readily replaced by heavy metals. Oxidising agents convert them into ethylene sulphonic acids, the group SH being oxidised to $SO_2.OH$.

Ethylene disulphhydrate, ethylene dimercaptan, ethylene thio-glycol, $C_2H_4(SH)_2$, prepared from ethylene dibromide and potassic sulphhydrate:



$$\begin{array}{l}CH_2.Br\\ |\\ CH_2.Br\end{array} + 2KSH = 2KBr + \begin{array}{l}CH_2.SH\\ |\\ CH_2.SH\end{array}$$

is a colourless, strongly refractive oil, of penetrating mercaptan-like odour, which boils at 146°. It gives precipitates with alcoholic solutions of silver, copper, lead, and mercury, &c., salts; plumbic acetate, for instance, precipitating yellow plumbic ethylene mercaptate:

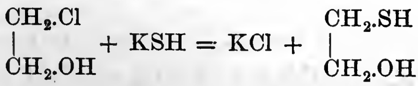


$$\begin{array}{l}CH_2.S\\ |\\ CH_2.S\end{array}\!\!>Pb.$$

Ethylene hydrate sulphhydrate, ethylene monothio-glycol:

$$C_2H_4(OH)(SH),$$

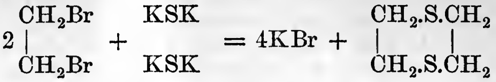
is obtained from ethylene chloro-hydrate:



$$\begin{array}{l}CH_2.Cl\\ |\\ CH_2.OH\end{array} + KSH = KCl + \begin{array}{l}CH_2.SH\\ |\\ CH_2.OH\end{array}$$

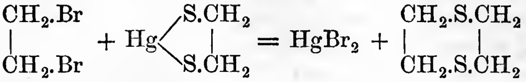
It is a colourless, heavy liquid, insoluble in water, only *one* hydrogen atom of which is readily replaced by metals.

510. *Ethylene Sulphide.*—Ethylene sulphide has as yet only been obtained in the double molecule corresponding to diethylene dioxide as *diethylene disulphide*, best by mixing alcoholic solutions of ethylene dihaloids with potassic sulphide:



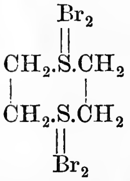
$$2\begin{array}{l}CH_2Br\\|\\CH_2Br\end{array} + \begin{array}{l}KSK\\ \\KSK\end{array} = 4KBr + \begin{array}{l}CH_2.S.CH_2\\|\qquad\quad|\\CH_2.S.CH_2\end{array}$$

It is also obtained by decomposing mercuric ethylene mercaptate by ethylene dibromide:



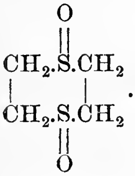
$$\begin{array}{l}CH_2.Br\\|\\CH_2.Br\end{array} + Hg\begin{array}{l}\diagup S.CH_2\\ \qquad|\\ \diagdown S.CH_2\end{array} = HgBr_2 + \begin{array}{l}CH_2.S.CH_2\\|\qquad\quad|\\CH_2.S.CH_2\end{array}$$

It is a white, crystalline mass, insoluble in water, but soluble in alcohol and ether, which melts at 111° and boils at 200°. The vapour density is found to be 4·28, corresponding to the formula $(C_2H_4)_2S_2$. It unites directly with bromine to yellow crystals of *diethylene disulphide tetrabromide*,



$$\begin{array}{c}Br_2\\ \|\\ CH_2.S.CH_2\\ |\qquad\quad|\\ CH_2.S.CH_2\\ \|\\ Br_2\end{array}$$

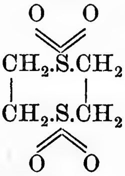
(comp. § 241), which on treatment with water and argentic oxide is converted into *diethylene dithionyl*,



$$\begin{array}{c}O\\ \|\\ CH_2.S.CH_2\\ |\qquad\quad|\\ CH_2.S.CH_2\\ \|\\ O\end{array}$$

. This body is also obtained on boiling the sulphide with nitric acid. It forms colourless crystals, readily soluble in water, little in alcohol, and insoluble in ether.

By heating the sulphide to 150° with nitric acid *diethylene sulphone* is formed (comp. § 255):



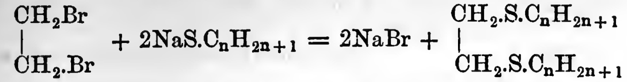
$$\begin{array}{c}O\quad O\\ \diagdown\diagup\\ CH_2.S.CH_2\\ |\qquad\quad|\\ CH_2.S.CH_2\\ \diagup\diagdown\\ O\quad O\end{array}$$

in the form of colourless crystals.

If ethylene gas be conducted into liquid sulphur dichloride, they both unite to a liquid of mustard-like odour of the formula $C_2H_4SCl_2$, probably $C_2H_4{<}{\begin{array}{l}Cl\\SCl\end{array}}$. This is not volatile unaltered, blisters the skin, dissolves in fifty volumes of ether, very little in alcohol, and is insoluble in water. Isoamylene also gives a similar compound.

Ethylene persulphides are obtained as white amorphous bodies by the action of ethylene dibromide upon the persulphides of potassium. They are insoluble in water and alcohol, but dissolve in carbonic disulphide.

511. *Thio-ethers of Ethylene.*—The thio-ethers of ethylene are obtained by action of ethylene dibromide on sodic thio-alkylates as unpleasant-smelling oils:



$$\begin{array}{l} CH_2Br \\ | \\ CH_2.Br \end{array} + 2NaS.C_nH_{2n+1} = 2NaBr + \begin{array}{l} CH_2.S.C_nH_{2n+1} \\ | \\ CH_2.S.C_nH_{2n+1} \end{array}$$

Ethylene dithio-methyl ether, $C_2H_4(S.CH_3)_2$, boils at 183°.

Ethylene dithio-ethyl ether, $C_2H_4(S.C_2H_5)_2$, boils at 210°–213°.

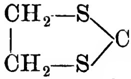
Ethylene dithio-isoamyl ether, $C_2H_4(S.C_5H_{11})_2$, boils between 245° and 255°.

The methyl compound, when heated with nitric acid, yields

Ethylene dimethyl dithionyl, $C_2H_4[(SO)CH_3]_2$, crystallising in brilliant plates, which melt at about 170°.

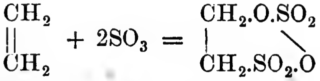
512. Of the *thio-salts* of ethylene the following may be mentioned:—

Ethylene disulpho-cyanate, $C_2H_4(S.CN)_2$, readily formed by boiling ethylene dihaloids with alcoholic solution of potassic sulpho-cyanate. It crystallises in colourless, brilliant, rhombic tables, melting at 90°. It is decomposed on strong heating, and is but little soluble in cold water.

Ethylene sulpho-carbonate,  $\begin{array}{l} CH_2—S \\ | \\ CH_2—S \end{array} \!\!> CS$, is formed by double decomposition of ethylene dibromide and sodic sulpho-carbonate in alcoholic solution. It separates at first as a yellow oil, difficultly soluble in alcohol, but after solution in ether alcohol and evaporation crystallises in golden yellow prisms of onion-like odour. It melts at 36·5°, and yields with ammonia, glycol-mercaptan and ammonic sulpho-cyanate.

Ethylene Sulphonic Acids.

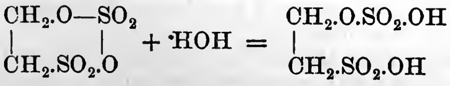
513. Ethylene gas and sulphuric anhydride unite directly to form *ethionic anhydride*:



$$\begin{array}{l} CH_2 \\ \| \\ CH_2 \end{array} + 2SO_3 = \begin{array}{l} CH_2.O.SO_2 \\ | \quad \diagdown \\ CH_2.SO_2.O \end{array}$$

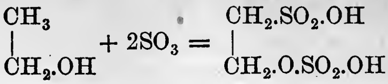
a colourless crystalline body, which unites the properties of a salt and of a sulphonic sulphuric anhydride. It is also obtained, together with diethylic sulphate and ethionic acid, by the action of ethylic alcohol vapour on sulphuric anhydride.

It absorbs water from moist air, and deliquesces to ethionic acid:



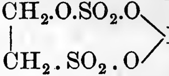
$$\begin{array}{l} CH_2.O—SO_2 \\ | \qquad\quad | \\ CH_2.SO_2.O \end{array} + HOH = \begin{array}{l} CH_2.O.SO_2.OH \\ | \\ CH_2.SO_2.OH \end{array}$$

This latter, which is at once ethylenic hydric sulphate and ethylene sulphonic acid, is obtained in larger quantity by saturating absolute alcohol or ethylic ether with sulphuric anhydride :

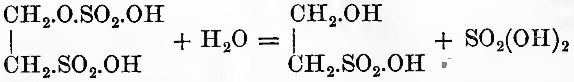


$$\begin{array}{l}CH_3\\|\\CH_2.OH\end{array} + 2SO_3 = \begin{array}{l}CH_2.SO_2.OH\\|\\CH_2.O.SO_2.OH\end{array}$$

The product is diluted with water, and the solution neutralised with baric carbonate to remove sulphuric acid and ethylic sulphate. *Baric ethionate,*



$\begin{array}{l}CH_2.O.SO_2.O\\|\\CH_2.SO_2.O\end{array}\!\!>Ba$, remains dissolved, and on addition of alcohol is precipitated as a white powder. By addition of the requisite quantity of sulphuric acid to the aqueous solution a solution of *ethionic acid* is obtained, which, on evaporation, decomposes into *isethionic acid* and sulphuric acid :



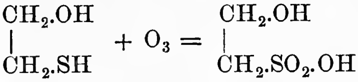
$$\begin{array}{l}CH_2.O.SO_2.OH\\|\\CH_2.SO_2.OH\end{array} + H_2O = \begin{array}{l}CH_2.OH\\|\\CH_2.SO_2.OH\end{array} + SO_2(OH)_2$$

Potassic ethionate, $KO.SO_2.O.CH_2.CH_2.SO_2.OK$, obtained by addition of potassic sulphate to the baric salt, crystallises readily. All the salts decompose on boiling with water into hydric sulphates and isethionates.

514. *Isethionic acid, ethylene hydrate sulphonic acid:*

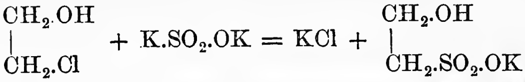
$$HO.CH_2.CH_2.SO_2.OH,$$

is obtained in addition to the above-mentioned methods by oxidation of ethylene monothio-glycol (§ 509) with nitric acid :



$$\begin{array}{l}CH_2.OH\\|\\CH_2.SH\end{array} + O_3 = \begin{array}{l}CH_2.OH\\|\\CH_2.SO_2.OH\end{array}$$

and further by heating ethylene hydrate chloride with normal potassic sulphite :



$$\begin{array}{l}CH_2.OH\\|\\CH_2.Cl\end{array} + K.SO_2.OK = KCl + \begin{array}{l}CH_2.OH\\|\\CH_2.SO_2.OK\end{array}$$

It is obtained most readily by addition of sulphuric anhydride to well-cooled anhydrous ether. After saturation the thick liquid is diluted with water, and boiled for several hours, in order to decompose the ethionic acid. The solution contains, together with some methionic acid (§ 419), isethionic acid and sulphuric acid. The latter is removed on saturating with baric carbonate. The liquid filtered at the boiling point first yields, on cooling, crystals of baric methionate, and later, on evaporation, *baric isethionate,* $(HO.CH_2.CH_2.SO_2.O)_2Ba$. If the solution of the latter be precipitated by sufficient sulphuric acid, and the filtrate evaporated, *isethionic acid* is obtained in strongly acid deliquescent needles.

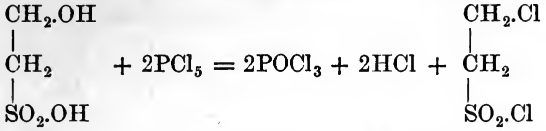
The isethionates, which can be prepared from the baric salt by addition of the respective metallic sulphates, are readily soluble in water, less in alcohol, crystallise well, and in most cases can be heated to 350° without decomposition.

Isethionic acid as a sulphonic acid is distinguished from the isomeric monethylic sulphate:

$$\mathrm{C_2H_6SO_4 = \underset{Monethylic\ sulphate.}{C_2H_5.O.SO_2.OH}\ and\ \underset{Isethionic\ acid.}{HO.C_2H_4.SO_2.OH}.}$$

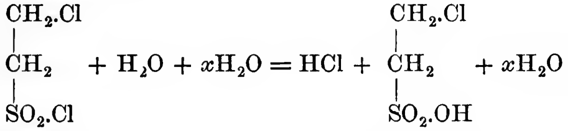
by its greater stability.

515. Dry potassic isethionate readily reacts with phosphoric chloride, forming hydrochloric acid, phosphoric oxychloride, and *isethionic chloride* or *ethylene sulphon chloride*:



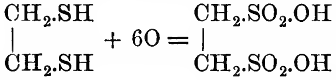
$$\begin{array}{l}\mathrm{CH_2.OH}\\ |\\ \mathrm{CH_2}\\ |\\ \mathrm{SO_2.OH}\end{array} + \mathrm{2PCl_5 = 2POCl_3 + 2HCl} + \begin{array}{l}\mathrm{CH_2.Cl}\\ |\\ \mathrm{CH_2}\\ |\\ \mathrm{SO_2.Cl}\end{array}$$

The latter boils at 200°, and combines the properties of an alcohol radical chloride with those of an acid radical chloride, only the latter being attacked on boiling with water and formation of *ethylene chloro-sulphonic acid*:



$$\begin{array}{l}\mathrm{CH_2.Cl}\\ |\\ \mathrm{CH_2}\\ |\\ \mathrm{SO_2.Cl}\end{array} + \mathrm{H_2O} + x\mathrm{H_2O = HCl} + \begin{array}{l}\mathrm{CH_2.Cl}\\ |\\ \mathrm{CH_2}\\ |\\ \mathrm{SO_2.OH}\end{array} + x\mathrm{H_2O}$$

516. *Ethylene disulphonic acid*, or *disulphethiolic acid*, is formed by the oxidation of ethylene dithio-glycol, ethylene sulpho-carbonate, and of ethylene dithio-cyanate with concentrated nitric acid:

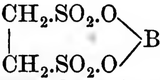


$$\begin{array}{l}\mathrm{CH_2.SH}\\ |\\ \mathrm{CH_2.SH}\end{array} + \mathrm{6O} = \begin{array}{l}\mathrm{CH_2.SO_2.OH}\\ |\\ \mathrm{CH_2.SO_2.OH}\end{array}$$

further by decomposition of propionitril by concentrated sulphuric acid, and by boiling ethylene dibromide with normal potassic sulphite:

$$\mathrm{C_2H_4Br_2 + 2K.SO_2.OK = 2KBr + C_2H_4(SO_2.OK)_2.}$$

Separated from its lead salt by hydric sulphide, or from its baric salt by sulphuric acid, it is obtained on evaporation of the solution in form of colourless crystals, melting at 94° and readily soluble in water.



The baric salt, $\left.\begin{array}{l}\mathrm{CH_2.SO_2.O}\\ |\\ \mathrm{CH_2.SO_2.O}\end{array}\right\rangle\mathrm{Ba}$, crystallises in hexagonal tables, insoluble in concentrated nitric acid, but can be recrystallised from boiling dilute nitric acid and is also soluble in water.

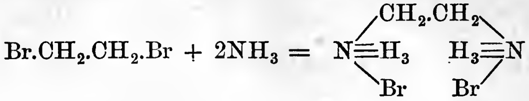
NITROGEN COMPOUNDS OF ETHYLENE.

Amine Bases of Ethylene.

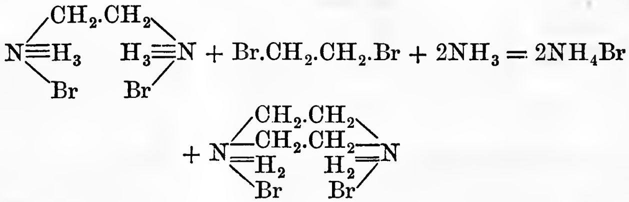
517. In the action of ethylene haloids upon ammonia, or the alkylamine bases, similar reactions occur to those in the formation of the alkylamines, but—in consequence of the divalency of ethylene

—with far greater complications of the products simultaneously formed. Of these only the simpler and more important will be mentioned.

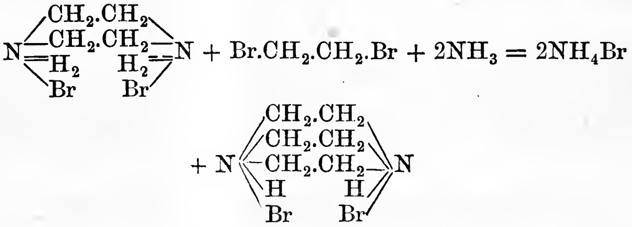
518. On heating ethylene dibromide with alcoholic ammonia there are principally formed, in consequence of the union of ethylene with the nitrogen of two ammonia groups, the hydro-bromides of the *ethylene diamine* bases. The first and simplest reaction yields, by direct union of a molecule of $C_2H_4Br_2$ with two molecules NH_3, *ethylene diammonic dibromide* :



The process, however, does not stop at this stage, but proceeds further:



and



diethylene diammonic dibromide and *triethylene diammonic dibromide* being simultaneously formed.

Ammonic bromide first crystallises out of the solution, then ethylene diammonic dibromide, and later follow the other salts.

If the whole mass of salts obtained by evaporation be distilled with solution of potassic hydrate:

$$C_2H_4(NH_3Br)_2 + 2KOH = 2KBr + 2H_2O + C_2H_4(NH_2)_2, \text{\&c.},$$

and the mixture of free amine bases dried by means of solid potassic hydrate, the single compounds can be separated on submitting to fractional distillation.

519. *Ethylene diamine*, $C_2H_4(NH_2)_2$, is a colourless, strongly alkaline liquid of faint ammoniacal odour, boiling at 123°, and has a vapour density of 2. It forms salts with two equivalents of acids. *Ethylene diammonic dichloride*, $C_2H_4(NH_2)_2Cl_2$, crystallises in beautiful needles of silvery lustre.

Another method of preparing ethylene diammonic dichloride consists in conducting cyanogen gas into hydrochloric acid in which granulated tin is dissolving :

$$\begin{array}{l}C\equiv N\\ |\\ C\equiv N\end{array} + 4Sn + 10HCl = 4SnCl_2 + \begin{array}{l}CH_2.NH_2.HCl\\ |\\ CH_2.NH_2.HCl\end{array}$$

Nitrous anhydride converts ethylene diamine into ethylene oxide, nitrogen being evolved :

$$\begin{array}{l}CH_2.NH_2\\ |\\ CH_2.NH_2\end{array} + N_2O_3 = 2H_2O + 2N_2 + \left.\begin{array}{l}CH_2\\ |\\ CH_2\end{array}\right\rangle O$$

By heating with ethylic iodide and decomposition of the product with potassic hydrate, ethyl groups can be introduced. In this way there have been prepared

Diethyl ethylene diamine, $C_2H_4[N(C_2H_5)H]_2$
and tetrethyl ethylene diamine, $C_2H_4[N(C_2H_5)_2]_2$.

The latter unites with ethylic iodide, forming

Hexethyl ethylene ammonic iodide, $\begin{array}{l}CH_2.N(C_2H_5)_3I\\ |\\ CH_2.N(C_2H_5)_3I\end{array}$

Ethylene diamine, diethyl ethylene diamine, &c., combine directly with a molecule of water to form ammonic oxides, which on evaporisation decompose into their constituents, but are again formed on condensation. The water is removed on distillation over fused potassic hydrate :

$$\begin{array}{l}CH_2.NH_2\\ |\\ CH_2.NH_2\end{array} + H_2O = \left.\begin{array}{l}CH_2.NH_3\\ |\\ CH_2.NH_3\end{array}\right\rangle O, \text{ ethylene diammonic oxide;}$$

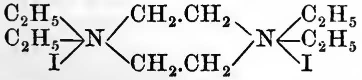
$$\begin{array}{l}CH_2.N(C_2H_5)H\\ |\\ CH_2.N(C_2H_5)H\end{array} + H_2O = \left.\begin{array}{l}CH_2.N(C_2H_5)H_2\\ |\\ CH_2.N(C_2H_5)H_2\end{array}\right\rangle O, \begin{array}{l}\text{diethyl-ethylene}\\ \text{diammonic oxide.}\end{array}$$

The latter solidifies to a stearine-like, brittle mass.

520. *Diethylene diamine*, $C_4H_{10}N_2$ or $NH\left\langle\begin{array}{l}C_2H_4\\ C_2H_4\end{array}\right\rangle NH$, is a colourless, liquid base, boiling at 170° and of vapour density 2·9.

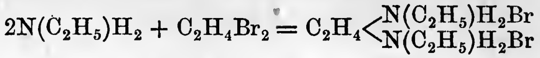
It unites directly with ethylic iodide, yielding diethyl-ethylene diammonic diiodide, from which alkalies separate

Diethyl-diethylene diamine, $C_2H_5.N\left\langle\begin{array}{l}C_2H_4\\ C_2H_4\end{array}\right\rangle N.C_2H_5$, as a volatile amine base; this further unites with two molecules of ethylic iodide, giving *tetrethyl diethylene diammonic diiodide* :



521. *Triethylene diamine*, $C_6H_{12}N_2 = N\left\langle\begin{array}{l}CH_2.CH_2\\ CH_2.CH_2\\ CH_2.CH_2\end{array}\right\rangle N$, is an oil boiling at 210°.

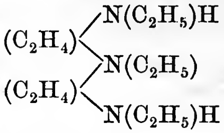
522. If ethylamine be heated with ethylene dibromide, there are formed, in addition to diethyl-ethylene diammonic dibromide and diethyl-diethylene diammonic dibromide:



$$2N(C_2H_5)H_2 + C_2H_4Br_2 = C_2H_4 \begin{cases} N(C_2H_5)H_2Br \\ N(C_2H_5)H_2Br \end{cases}$$

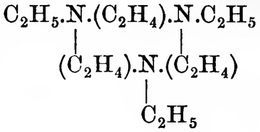
also bromides of other ammonium bases, containing more than two nitrogen atoms. Decomposed by potassic hydrate, there pass over, above 200°, strongly caustic thick-liquid compounds which are soluble in water, and from whose mixture

triethyl-diethylene triamine,



$$\begin{matrix} & N(C_2H_5)H \\ (C_2H_4) & \\ & N(C_2H_5) \\ (C_2H_4) & \\ & N(C_2H_5)H \end{matrix}$$

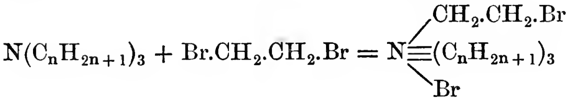
and triethyl-triethylene tetramine,



$$\begin{matrix} C_2H_5.N.(C_2H_4).N.C_2H_5 \\ | \qquad\qquad | \\ (C_2H_4).N.(C_2H_4) \\ | \\ C_2H_5 \end{matrix}$$

can be isolated. These give salts with two or three equivalents of acid.

523. By the action of trialkylamine bases upon ethylene dibromide, trialkyl-ethylene bromide ammonic bromides are formed:

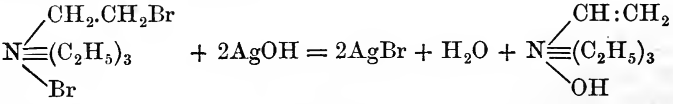


$$N(C_nH_{2n+1})_3 + Br.CH_2.CH_2.Br = N \begin{cases} CH_2.CH_2.Br \\ \equiv (C_nH_{2n+1})_3 \\ Br \end{cases}$$

Triethylamine and ethylene bromide, e.g., give *triethyl-ethylene bromide ammonic bromide*, $N(C_2H_5)_3(C_2H_4Br)Br$. With argentic nitrate it yields *triethyl-ethylene bromide ammonic nitrate:*

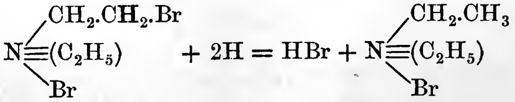
$$[N(C_2H_5)_3(C_2H_4Br)]O.NO_2.$$

By treatment with argentic oxide and water all bromine is removed and replaced, as far as regards that united to nitrogen, by hydroxyl, whilst the ethylene mono-bromide group loses an atom of hydrogen also, and is converted into vinyl, $CH_2{:}CH$. There thus results *triethyl-vinyl ammonic hydrate:*



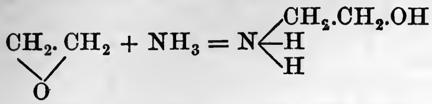
$$N \begin{cases} CH_2.CH_2Br \\ \equiv (C_2H_5)_3 \\ Br \end{cases} + 2AgOH = 2AgBr + H_2O + N \begin{cases} CH{:}CH_2 \\ \equiv (C_2H_5)_3 \\ OH \end{cases}$$

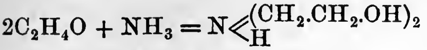
By nascent hydrogen the ethylene bromide group is converted into ethyl, and tetrethyl ammonic bromide is formed:



$$N \begin{cases} CH_2.CH_2.Br \\ \equiv (C_2H_5) \\ Br \end{cases} + 2H = HBr + N \begin{cases} CH_2.CH_3 \\ \equiv (C_2H_5) \\ Br \end{cases}$$

524. The ethylene hydrate amines are closely related to the ethylene monobromo-bases. In these ethylene is united by one bond with OH, and by its second bond to an ammonia residue. These strongly basic ethylene hydrate amines are formed by the combination of ethylene oxide with concentrated solution of ammonia or substituted amines, the reactions being violent:


ethylene hydrate amine;

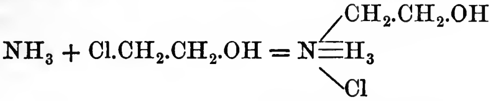


$$2C_2H_4O + NH_3 = N\left\langle\begin{matrix}(CH_2.CH_2.OH)_2\\ H\end{matrix}\right.$$

diethylene hydrate amine;

$$3C_2H_4O + NH_3 = N\equiv(CH_2.CH_2.OH)_3,$$ triethylene hydrate amine.

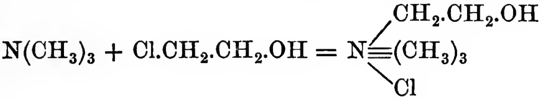
In the form of their salts they are obtained by bringing together ethylene hydrate chloride and ammonia or amine bases, only one molecule, however, generally entering into reaction:



$$NH_3 + Cl.CH_2.CH_2.OH = N\left\langle\begin{matrix}CH_2.CH_2.OH\\ \equiv H_3\\ Cl\end{matrix}\right.$$

Ethylene hydrate ammonic chloride.

and



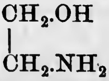
$$N(CH_3)_3 + Cl.CH_2.CH_2.OH = N\left\langle\begin{matrix}CH_2.CH_2.OH\\ \equiv(CH_3)_3\\ Cl\end{matrix}\right.$$

Ethylene hydrate trimethyl ammonic chloride,
or choline hydrochloride.

They are, therefore, half alcohols and half animes.

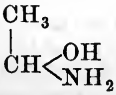
In order to separate the compounds simultaneously formed, the varying solubility of their hydrochlorides and platino-chlorides is made use of. The mixture, after addition of hydrochloric acid, is evaporated as far as possible to dryness, whereby *triethylene hydrate ammonic chloride*, $N(C_2H_4.OH)_3.HCl$, partly crystallises out in prisms, whilst *diethylene hydrate* and *monethylene hydrate ammonic chlorides* cannot be obtained in the solid state. The first is insoluble in absolute alcohol, which dissolves both the others; the alcoholic solution is then mixed with platinic chloride. The double salt of *diethylene hydrate ammonic chloride*, $[N(C_2H_4.OH)_2H_2Cl]_2PtCl_4$, crystallising in prisms, first separates, whilst that of *ethylene hydrate ammonic chloride*, $[N(C_2H_4.OH)H_3Cl]_2PtCl_4$, is precipitated later on addition of ether. The platino-chlorides are separated, dissolved in water, and the platinum precipitated by hydric sulphide. On evaporation the hydrochlorides are obtained, which by treatment with moist argentic oxide yield the free bases. The latter are strongly alkaline syrups, which dissolve in alcohol.

Monethylene hydrate amine is isomeric with aldehyde ammonia or ethylidene hydrate amine (§ 424):



$$\begin{matrix}CH_2.OH\\ |\\ CH_2.NH_2\end{matrix}$$

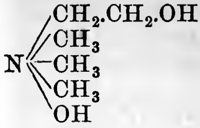
Ethylene hydrate amine.



$$\begin{matrix}CH_3\\ |\\ CH\left\langle\begin{matrix}OH\\ NH_2\end{matrix}\right.\end{matrix}$$

Ethylidene hydrate amine.

525. *Choline*, $C_5H_{15}NO_2$, *trimethyl ethylene hydrate ammonic hydrate :*



$$N\begin{cases}CH_2.CH_2.OH\\CH_3\\CH_3\\CH_3\\OH\end{cases}$$

requires more detailed notice.

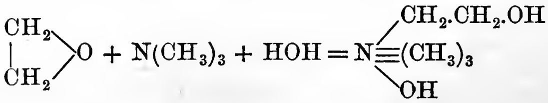
This strongly alkaline ammonium base was first found in the bile, later prepared under the name *neurine* from the brain, and also occurs widely diffused in organic nature as '*sincaline*.' Neurine does not occur as such in the organism, but in combination forming *lecithine*, a fatty substance, which yields neurine as a product of its resolution into simpler bodies.

In order to prepare choline, ox brain is generally employed. This is finely divided, and extracted first by frequent shaking with ether and then with warm alcohol. The ether and alcohol are then evaporated off, and the residue boiled for about an hour with excess of solution of baric hydrate. Excess of baric hydrate is then removed by passing carbonic anhydride, the liquid boiled, filtered, and the clear aqueous liquid evaporated to a syrup on the water bath. This is extracted with absolute alcohol, the filtered solution treated with slight excess of hydrochloric acid and precipitated with platinic chloride. The clear yellow precipitate of platino-chloride is then dissolved in water, freed from platinum by hydric sulphide, and finally crystalline choline hydrochloride, $N(CH_3)_3(C_2H_4.OH).Cl$, obtained by evaporation in a dry vacuum. This, on treatment with moist argentic oxide, yields an aqueous solution of free neurine :

$$N(CH_3)_3(C_2H_4.OH)Cl + AgOH = AgCl + N(CH_3)_3(C_2H_4.OH)OH,$$

which, on complete evaporation, forms a caustic, alkaline, difficultly soluble syrup, which absorbs water and carbonic anhydride from the air. The platino-chloride, $[N(CH_3)_3(C_2H_4.OH)Cl]_2PtCl_4$, crystallises from its aqueous solution in beautiful reddish yellow tables. According to some authors, the base obtained from nervous tissue is not choline, but *trimethyl-vinylammonic hydrate*, which they then term *neurine*. But, as hydrochloric acid is employed in the preparation, it may readily have occurred that trimethyl-ethylene chloride ammonic chloride may have been formed, which would yield the vinyl base when treated with argentic oxide.

Choline is obtained synthetically by the action of ethylene hydrate chloride or of ethylene oxide and water on trimethylamine:



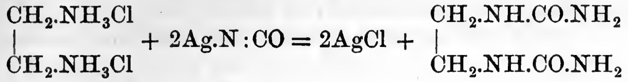
$$\left.\begin{matrix}CH_2\\|\\CH_2\end{matrix}\right\rangle O + N(CH_3)_3 + HOH = N\begin{cases}CH_2.CH_2.OH\\(CH_3)_3\\OH\end{cases}$$

On heating choline with concentrated hydriodic acid and some red phosphorus at 140° it yields *trimethyl-ethylene iodo-ammonic iodide*, $N(CH_3)_3(C_2H_4I)I$, which is also obtained from trimethylamine and ethylene diiodide. Moist argentic oxide converts it into *trimethyl-vinylammonic hydrate :*

$$N(CH_3)_3(C_2H_4I)I + 2AgOH = 2AgI + H_2O$$
$$+ N(CH_3)_3CH{:}CH_2.OH.$$

526. *Urea Derivatives.*—On heating ethylene diammonic chloride with argentic cyanate, and evaporating the filtered liquid, crystals are obtained of

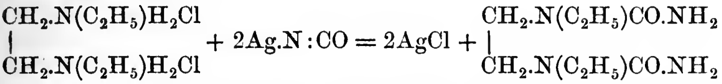
Ethylene diurea, $C_4H_{10}N_4O_2$:



$$\begin{array}{l}CH_2.NH_3Cl\\ |\\ CH_2.NH_3Cl\end{array} + 2Ag.N{:}CO = 2AgCl + \begin{array}{l}CH_2.NH.CO.NH_2\\ |\\ CH_2.NH.CO.NH_2\end{array}$$

This is difficultly soluble in cold water and alcohol, melts at 192°, combines with acids to form salts, and on heating with potassic hydrate yields ammonia, ethylene diamine, and potassic carbonate.

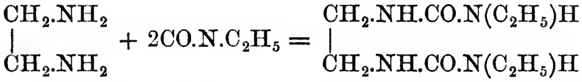
Diethyl-ethylene diurea, $C_6H_{18}N_4O_2$, is obtained similarly to the foregoing from diethyl ethylene ammonic dichloride and argentic pseudo-cyanate:



$$\begin{array}{l}CH_2.N(C_2H_5)H_2Cl\\ |\\ CH_2.N(C_2H_5)H_2Cl\end{array} + 2Ag.N{:}CO = 2AgCl + \begin{array}{l}CH_2.N(C_2H_5)CO.NH_2\\ |\\ CH_2.N(C_2H_5)CO.NH_2\end{array}$$

It is readily soluble in alcohol, and is readily decomposed on heating with acids, yielding carbonic anhydride and salts of diethyl ethylene diamine and ammonia.

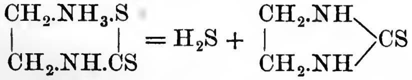
Ethylene diethyl-urea, $C_6H_{18}N_4O_2$, isomeric with the preceding, is obtained by the action of diethylene diamine on ethylic pseudo-cyanate:



$$\begin{array}{l}CH_2.NH_2\\ |\\ CH_2.NH_2\end{array} + 2CO.N.C_2H_5 = \begin{array}{l}CH_2.NH.CO.N(C_2H_5)H\\ |\\ CH_2.NH.CO.N(C_2H_5)H\end{array}$$

It is insoluble in alcohol and is difficultly decomposed by strong acids, but on heating with alkalies gives carbonates, ethylamine, and ethylene diamine.

527. *Ethylene dithio-urea* can be obtained from ethylene diamine and carbonic disulphide in the following way (comp. § 284):—On mixing in presence of alcohol, the mixture, at first clear, solidifies to a mass insoluble in alcohol and ether, containing equal molecules of the two ingredients. On boiling the aqueous solution for a long time, hydric sulphide is evolved, and on cooling fine white crystals of bitter taste separate of *ethylene sulphurea,* $C_3H_6N_2S$:

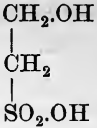


$$\begin{array}{lr}CH_2.NH_3.S & \\ | & |\\ CH_2.NH.CS & \end{array} = H_2S + \begin{array}{l}CH_2.NH\\ |\\ CH_2.NH\end{array}\!\!>CS$$

It yields very unstable salts with acids, but is precipitated by mercuric chloride and argentic nitrate as crystalline compounds with these salts; e.g. $2C_3H_6N_2S,3HgCl_2$.

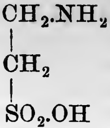
Taurine, $C_2H_7NSO_3$.

528. *Taurine,* or *ethylene-amine sulphonic acid,* stands in close relationship to isethionic acid:



$$\begin{array}{l} CH_2.OH \\ | \\ CH_2 \\ | \\ SO_2.OH \end{array}$$

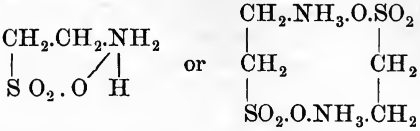
Isethionic acid.



$$\begin{array}{l} CH_2.NH_2 \\ | \\ CH_2 \\ | \\ SO_2.OH \end{array}$$

Taurine.

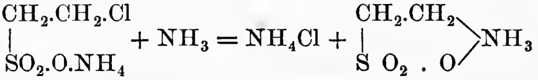
It is of great physiological importance. As this compound is at the same time a sulphonic acid and an amine, it can only exist as a saline compound, which may be derived from only one molecule, but more probably possesses the double formula :



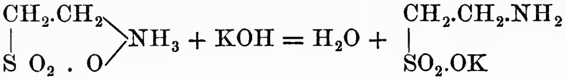
Taurine is most readily prepared from the bile of animals, which contains invariably the alkaline salts of nitrogenous and sulphur-containing acids, taurocholic acids. The latter are converted into sulphur-free acids (cholic acids) and taurine on boiling with strong acids or bases (comp. bile acids).

Taurine is also found in animal tissues, e.g. in the lungs and muscles (especially of mollusca).

It is prepared synthetically by heating ammonic ethylene chlorosulphonate with aqueous ammonia to 100° :

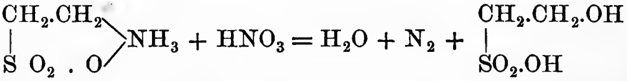


Taurine crystallises in large, hard, colourless prisms of the monoclinic system, without taste or odour, and which are difficultly soluble in cold, readily in hot water, insoluble in alcohol and ether. With potassic hydrate it yields potassic ethylene-amine sulphonate :



which is of alkaline reaction and is soluble in alcohol.

By action of nitrous acid taurine is converted into isethionic acid, nitrogen being evolved :



Nitryl Compounds of the Olefines.

529. Compounds of the glycol radicals with nitryl, (NO_2), have only as yet been obtained from the olefines by action of concentrated nitric acid or by direct union with nitric peroxide.

Ethylene dinitryl, $C_2H_4N_2O_4$, is most readily obtained when dry ethylene gas is passed into anhydrous ether, to which, at the same time, liquid nitric peroxide is added drop by drop :

$$C_2H_4 + N_2O_4 = C_2H_4(NO_2)_2.$$

Colourless prisms or tables of ethylene dinitryl separate, which melt at 37·5°, and volatilise at slightly higher temperature (with especial readiness in an atmosphere of ethylene gas).

Isoamylene dinitryl, $C_5H_{10}(NO_2)_2$, is obtained by passing nitric peroxide vapour into isoamylene, or isoamylene vapour into red fuming nitric acid. It crystallises in rectangular tables, which decompose at 95°, but sublime slowly below this temperature.

Phosphorus and Arsenic Compounds of Ethylene.

530. Triethyl phosphine and triethyl arsine behave towards ethylene haloids in similar manner to the trialkylamines (§ 522).

1. If triethyl-phosphine be left for a long time with ethylene dibromide at ordinary temperatures, it yields mainly

Triethyl-ethylene bromo-phosphonic bromide:

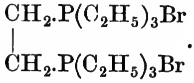
$$C_8H_{19}PBr_2 = P(C_2H_5)_3(CH_2.CH_2Br)Br,$$

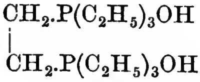
crystallising from water and alcohol in rhombic dodecahedrons. On addition of argentic nitrate half the bromine is precipitated, whilst the nitrate, $P(C_2H_5)_3(C_2H_4Br)O.NO_2$, remains in solution. The latter is converted by hydrochloric acid into the chloride, $P(C_2H_5)_3(C_2H_4Br)Cl$, which gives with platinic chloride a difficultly soluble double salt, crystallising in long prisms.

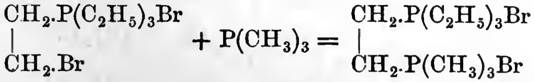
If the original bromide be heated, either alone or with argentic salts, it loses hydrobromic acid from the ethylene bromide group, and yields derivatives of *triethyl-vinyl phosphonium*; on heating to 240°, e.g., a residue of *triethyl-vinyl phosphonic bromide*, $P(C_2H_5)_3(C_2H_3)Br$, remains.

If, on the other hand, the first bromide be heated in dilute solution with argentic oxide, both bromine atoms are replaced by hydroxyl, and the strongly alkaline base *triethyl-ethylene hydrate phosphonic hydrate*, $P(C_2H_5)_3(CH_2.CH_2\,OH)OH$, is obtained.

2. An excess of triethyl-phosphine is converted by ethylene dibromide into

Hexethyl-ethylene diphosphonic dibromide,

$\begin{array}{l} CH_2.P(C_2H_5)_3Br \\ | \\ CH_2.P(C_2H_5)_3Br \end{array}$. This crystallises in colourless needles readily soluble in alcohol and water. By moist argentic oxide it is converted into

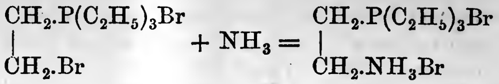
Hexethyl-ethylene diphosphonic dihydrate,

$\begin{array}{l} CH_2.P(C_2H_5)_3OH \\ | \\ CH_2.P(C_2H_5)_3OH \end{array}$, a strongly caustic, deliquescent mass. Triethyl-ethylene bromide phosphonic bromide also gives analogous derivatives with trialkyl phosphines:



$$\begin{array}{l} CH_2.P(C_2H_5)_3Br \\ | \\ CH_2.Br \end{array} + P(CH_3)_3 = \begin{array}{l} CH_2.P(C_2H_5)_3Br \\ | \\ CH_2.P(CH_3)_3Br \end{array}$$

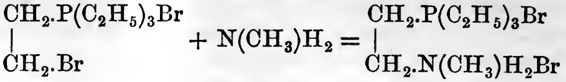
Trimethyl-triethyl diphosphonic dibromide.

531. The latter reaction can be employed for the preparation of compounds containing both phosphorus and nitrogen:



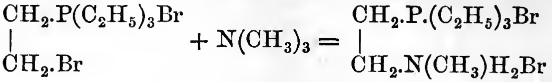
$$\begin{array}{l}\mathrm{CH_2.P(C_2H_5)_3Br}\\ |\\ \mathrm{CH_2.Br}\end{array} + \mathrm{NH_3} = \begin{array}{l}\mathrm{CH_2.P(C_2H_5)_3Br}\\ |\\ \mathrm{CH_2.NH_3Br}\end{array}$$

Triethyl-ethylene phosphammonic dibromide.



$$\begin{array}{l}\mathrm{CH_2.P(C_2H_5)_3Br}\\ |\\ \mathrm{CH_2.Br}\end{array} + \mathrm{N(CH_3)H_2} = \begin{array}{l}\mathrm{CH_2.P(C_2H_5)_3Br}\\ |\\ \mathrm{CH_2.N(CH_3)H_2Br}\end{array}$$

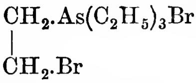
Triethyl-methyl ethylene phosphammonic dibromide.



$$\begin{array}{l}\mathrm{CH_2.P(C_2H_5)_3Br}\\ |\\ \mathrm{CH_2.Br}\end{array} + \mathrm{N(CH_3)_3} = \begin{array}{l}\mathrm{CH_2.P.(C_2H_5)_3Br}\\ |\\ \mathrm{CH_2.N(CH_3)H_2Br}\end{array}$$

&c. Triethyl-trimethyl ethylene phosphammonic dibromide.

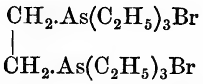
532. Triethylarsine behaves towards ethylene dibromide in similar manner, and yields arsonic derivatives analogous to the phosphonic derivatives (§ 530) :



$$\begin{array}{l}\mathrm{CH_2.As(C_2H_5)_3Br}\\ |\\ \mathrm{CH_2.Br}\end{array}$$

Triethyl-ethylene bromide arsonic bromide.

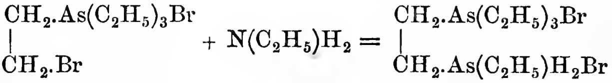
and



$$\begin{array}{l}\mathrm{CH_2.As(C_2H_5)_3Br}\\ |\\ \mathrm{CH_2.As(C_2H_5)_3Br}\end{array}$$

Hexethyl-ethylene diarsonic dibromide.

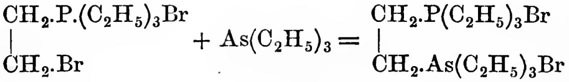
of which the first unites directly with ammonia, amines, and phosphines; e.g.



$$\begin{array}{l}\mathrm{CH_2.As(C_2H_5)_3Br}\\ |\\ \mathrm{CH_2.Br}\end{array} + \mathrm{N(C_2H_5)H_2} = \begin{array}{l}\mathrm{CH_2.As(C_2H_5)_3Br}\\ |\\ \mathrm{CH_2.As(C_2H_5)H_2Br}\end{array}$$

Triethyl-ethyl ethylene arsammonic dibromide.

Triethyl arsine also unites directly with triethyl-ethylene bromide phosphonic bromide :



$$\begin{array}{l}\mathrm{CH_2.P.(C_2H_5)_3Br}\\ |\\ \mathrm{CH_2.Br}\end{array} + \mathrm{As(C_2H_5)_3} = \begin{array}{l}\mathrm{CH_2.P(C_2H_5)_3Br}\\ |\\ \mathrm{CH_2.As(C_2H_5)_3Br}\end{array}$$

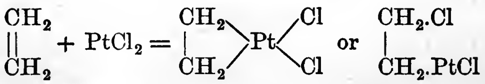
Hexethyl-ethylene phospharsonic dibromide.

&c.

Metallic Compounds of Ethylene.

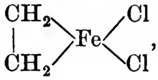
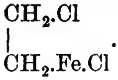
533. Glycol derivatives corresponding to the large group of metallic compounds of the monad alcohol radicals are not known. Their preparation has in part been attempted without result. Only ethylene forms some derivatives in which it is at least in part united to metals, especially platinum and iron.

Ethylene platinum chloride, $C_2H_4PtCl_2$, is formed by heating a solution of platinic chloride with alcohol, or by passing ethylene gas into a hydrochloric acid solution of platinous chloride :



It is a clear yellow mass, whose aqueous solution yields compounds with ammonic and potassic chlorides, crystallising in rhombic prisms.

The latter, $C_2H_4PtCl_2,KCl,H_2O$, yields on heating ethylene gas, whilst potassic platinous chloride remains. Propylene and isoamylene also yield similar compounds; $C_3H_6PtCl_2,KCl,H_2O$ crystallises in yellow tables; $C_5H_{10}PtCl_2,KCl,H_2O$, in golden yellow scales resembling plumbic iodide.

Ethylene iron chloride, $C_2H_4FeCl_2,2H_2O$. This body is obtained on heating a solution of ferric chloride in ether to 140°–150°, better if some phosphorus dissolved in carbonic disulphide be added, the heat of the water bath then sufficing. The liquid fills with hard, nearly colourless crystals of the above formula. These become somewhat damp in the air, and oxidise, turning yellow. They dissolve readily in water, and lose their water of crystallisation at 100°. Their whole behaviour characterises them as a ferrous compound, so that their composition cannot be expressed by the formula , but is in all probability  $\begin{array}{l} CH_2.Cl \\ | \\ CH_2.Fe.Cl \end{array}$. Their formation is expressed by the equation:

$$2(C_2H_5)_2O + Fe_2Cl_6 = 2C_2H_4FeCl_2 + 2C_2H_5.OH + 2Cl_2,$$

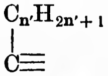
the chlorine acting on the resulting alcohol or the excess of ether either directly or after combination with phosphorus.

TRIPLE SUBSTITUTION PRODUCTS OF THE PARAFFINS.

DERIVATIVES OF THE TRIVALENT RADICALS, C_nH_{2n-1}.

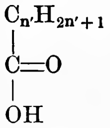
534. The replacement of three hydrogen atoms in a paraffin by other elements or compound radicals yields, in accordance with the chemical position of the replacement, the following groups of compounds :—

1. If the three substitution positions are on a single, necessarily terminal carbon atom, there occur derivatives of the hydrocarbon radical :



$$\begin{array}{l} C_{n'}H_{2n'+1} \\ | \\ C\equiv \end{array}$$

whose simplest oxygen compounds are the organic acids $C_nH_{2n}O_2$ or

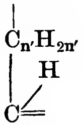


$$\begin{array}{l} C_{n'}H_{2n'+1} \\ | \\ C{=}O \\ | \\ OH \end{array}$$

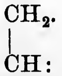
The first member of the series is the mono-carbonide formyl $H.C\vdots$

2. If two substitution positions occur on one, the third on a second carbon atom, two cases may occur.

a. The double replacement occurs, as in the aldehydes, on a terminal carbon atom :

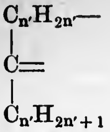


The compounds of this class are those of the *mono-substituted aldehyde radicals.* The first member of the series is a dicarbonide :



$$\begin{array}{l} CH_2. \\ | \\ CH: \end{array}$$

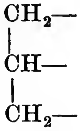
b. In the derivatives of the *mono-substituted ketone radicals* the double substitution has occurred on an intermediate secondarily united carbon atom:



$$\begin{array}{l} C_{n'}H_{2n'}— \\ | \\ C= \\ | \\ C_{n'}H_{2n'+1} \end{array}$$

All compounds of this class must contain more than two carbon atoms.

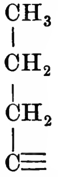
3. If, finally, all these substitution positions occur on three different carbon atoms, there result derivatives of the trivalent alcohol radicals, whose first member is the tricarbonide glyceryl or allyl:



$$\begin{array}{l} CH_2— \\ | \\ CH— \\ | \\ CH_2— \end{array}$$

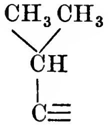
DERIVATIVES OF THE ACID RADICALS, $C_nH_{2n'+1}.C\vdots$.

535. The first member of this series, strictly speaking, is the radical of acetic acid, $CH_3.C\vdots$ (acetyl), but that of formic acid, $H.C\vdots$ (formyl), shows such analogy that it must be included in the group. Up to the tricarbon radical of propionic acid, $CH_3.CH_2.C\vdots$, no isomerism occurs, this commencing only with a carbon contents of four atoms:



$$\begin{array}{l} CH_3 \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ C\equiv \end{array}$$

and



Their number is always equal to the number of primary alcohols of equal carbon contents.

536. By far the larger number of the acid radical derivatives contain an oxygen atom in divalent union, oxidised radicals, $C_nH_{2n+1}.CO$, *acidoxyls*, thereby resulting, whose hydrates are the monobasic organic acids, $C_{n'}H_{2n'+1}.CO.OH$. In these hydrates not only the halogen atom, but also the whole hydroxyl group is readily replaced by other elements, whilst the oxygen atom in diad union is only eliminated or replaced with difficulty.

Halogen and Nitryl Compounds.

537. The number of known halogen compounds of the acidyl residue C_nH_{2n-1} is very small, consisting of the trihaloids of formyl and acetyl.

The trichlorides and tribromides are obtained directly by the action of the respective halogens upon the paraffins, but are more readily prepared from the chlorides and bromides of the respective primary alcohols and the dihaloids of the aldehyde radicals:

$$C_{n'}H_{2n'+1}.CH_2Cl + 2Cl_2 = C_{n'}H_{2n'+1}.CCl_3 + 2HCl$$
$$C_{n'}H_{2n'+1}.CHCl_2 + Cl_2 = C_{n'}H_{2n'+1}.CCl_3 + HCl.$$

They can be partly obtained from the acidoxyl chlorides, $C_{n'}H_{2n'+1}.COCl$, by heating with excess of phosphoric chloride:

$$C_{n'}H_{2n'+1}.COCl + PCl_5 = POCl_3 + C_{n'}H_{2n'+1}.CCl_3.$$

The yield, however, is but small, the high temperature required for the reaction leading to further decompositions.

Formyl Compounds.

538. *Formyl trichloride*, or *chloroform*, $CHCl_3$, trichlor methane. Chloroform is obtained by the direct action of chlorine gas on methane, methylic chloride, and methene dichloride, and further by the distillation of wood spirit, alcohol, acetone, acetates, and several other organic bodies with chloride of lime, also, together with potassic formate, by heating chloral with solution of potassic hydrate:

$$CCl_3.CHO + HOK = CCl_3H + CHO.OK.$$

The latter method has been employed of late for the manufacture of pure chloroform; in large quantity it is still obtained from alcohol. For this purpose three parts of alcohol, 100 parts of water, and fifty parts of chloride of lime are submitted to distillation. In the receiver, which must be kept well cooled, two layers of liquid collect, the under consisting mainly of chloroform. This is shaken with water and then purified by distillation over concentrated sulphuric acid.

Chloroform is a colourless, strongly refractive liquid, not miscible with water, of sp. gr. 1·52 at 0°, boiling point 61°, and of vapour density 4·199. It is uninflammable in air, has an agreeable odour, a sweet taste, and on long inhaling of its vapour produces loss of consciousness and insensibility to pain. It is therefore employed as an anæsthetic agent.

Chloroform is further employed as a solvent for fats, resins, caoutchouc, &c. Sulphur, phosphorus, and iodine also dissolve in it, the latter with violet colour.

Ammonia converts chloroform at 180° into ammonic chloride and cyanide:

$$HCCl_3 + 5NH_3 = 3NH_4Cl + (NH_4)CN;$$

by addition of potassic hydrate ammonic cyanide is obtained at considerably lower temperatures:

$$HCCl_3 + 2NH_3 + 3KOH = 3KCl + (NH_4)CN + 3H_2O.$$

Alcoholic potassic hydrate converts it into potassic chloride and formate:

$$HCCl_3 + 4HOK = 3KCl + HCO.OK + 2H_2O,$$

or in presence of alkylamines gives the alkyl isocyanates (§ 278).

The chloroform of commerce, especially when prepared from alcohol, is frequently contaminated with other bodies, such as alcohol, aldehyde, ethylidene dichloride, &c., and then readily becomes useless on keeping. Pure chloroform must be without action on vegetable colours, must not colour a mixture of sulphuric and chromic acids green, must not turn brown with sulphuric acid or potassic hydrate, and must not suddenly evolve inflammable gases (monochlor ethylene) when heated with alcoholic potassic hydrate.

By the action of chlorine on boiling chloroform in sunlight

Carbonic tetrachloride, or *tetrachlor methane*, CCl_4, is obtained as a colourless oil of ethereal odour, of sp. gr. 1·56 and of boiling point 78°. The same compound is formed by passing chlorine into a heated mixture of carbonic disulphide and antimonic chloride:

$$CS_2 + 6Cl = S_2Cl_2 + CCl_4.$$

The product is distilled, and that portion passing over below 100° treated with solution of potassic hydrate in order to decompose the sulphur chloride.

Potassic hydrate decomposes an alcoholic solution of carbonic tetrachloride into potassic chloride and carbonate:

$$CCl_4 + 6KOH = 4KCl + K_2CO_3 + 3H_2O;$$

and nascent hydrogen converts it into chloroform, methene dichloride, methylic chloride, and even methane:

$$CCl_4 + 2H = CHCl_3 + HCl, \&c.$$

Methane is also obtained when the vapour of tetrachlor methane mixed with hydrogen is passed through red-hot tubes:

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

539. *Formyl tribromide, bromoform*, $CHBr_3$, is obtained, similarly to chloroform, by the action of bromine and potassic hydrate upon methylic and ethylic alcohols, acetone, &c. It closely resembles chloroform, but has a higher sp. gr. (2·9), boils between 150° and 152°, and solidifies at −9° to a colourless crystalline mass.

On heating bromoform or carbonic disulphide with bromine, *carbonic tetrabromide*, CBr_4, is obtained; it melts at 92·5°, is insoluble in water, and forms tabular crystals.

540. *Formyl triiodide*, or *iodoform*, CH_3I, is obtained by heating methylic and ethylic alcohols, ether, acetone, sugar, dextrine, albuminoids, &c., with potassic hydrate and iodine. It separates thereby in yellow leafy crystals, which on recrystallisation from ether form large, citron-yellow, brilliant, hexagonal tables. It is insoluble in water, but readily soluble in alcohol and ether. At ordinary temperatures it evaporates slowly and smells like saffron. It evaporates readily and unchanged with aqueous vapour and melts at 119°. Its reactions resemble those of chloroform. Its convertibility into methene compounds has been already mentioned (§ 380).

If iodoform be distilled with plumbic, mercuric, or zinic chlorides, *formyl dichloroiodide*, or *dichloriodoform*, $CHCl_2I$, passes over as a yellow-coloured oil, boiling at 131°. Bromine converts iodoform into *formyl dibromiodide*, or *dibromiodoform*, $CHBr_2I$.

541. *Nitroform*, or *trinitro-methane*, $CH(NO_2)_3$, is formed by the action of the most concentrated nitric acid upon the bile acids, upon œnanthol, and some organic bodies. It is usually prepared from triaceto-nitrile (see later). On boiling this with water or alcohol, carbonic anhydride is evolved, and the solution evaporated on completion of the reaction yields yellow crystals of a saline ammonium derivative of nitroform :

$$C(NO_2)_3.CN + 2H_2O = C(NO_2)_3.NH_4 + CO_2.$$

On heating this latter with concentrated sulphuric acid, nitroform separates as a colourless oil, which crystallises on cooling :

$$C(NH_4)(NO_2)_3 + H_2SO_4 = (NH_4)HSO_4 + CH(NO_2)_3.$$

Trinitro-methane crystallises in colourless cubes, which melt at 15° to a liquid of powerful odour. It decomposes slowly at 100°, on quicker heating, with violent explosion.

Nitroform has the properties of a powerful acid, combines with ammonia, forming $C(NH_4)(NO_2)_3$, and yields yellow crystallisable salts with the alkalies :

$$CH(NO_2)_3 + KOH = CK(NO_2)_3 + H_2O.$$

A mixture of concentrated nitric and sulphuric acids converts it into *Tetranitro-methane :*

$$CH(NO_2)_3 + HO.NO_2 + H_2SO_4 = H_4SO_5 + C(NO_2)_4,$$

a colourless uninflammable oil, boiling at 126°, which solidifies in the cold to colourless crystals, melting at about 13°.

542. *Nitro-chloroform,* or *chloro-picrin,* $CCl_3(NO_2)$, is formed by the distillation of methylic or ethylic alcohol with sodic chloride, nitric acid, and sulphuric acid. It is formed from many chlorinated organic bodies by heating with concentrated nitric acid :

$$\underset{\text{Chloral.}}{CCl_3.CHO} + HO.NO_2 = CCl_3(NO_2) + H_2O + CO_2.$$

By heating chloroform with concentrated nitric and sulphuric acids, but little chloro-picrin is formed together with many gaseous products :

$$CHCl_3 + HONO_2 + H_2SO_4 = H_4SO_5 + C(NO_2)Cl_3.$$

It is most readily prepared by mixing one part of a solution of trinitrophenol (picric acid), saturated at 30°, with ten parts of bleaching powder rubbed up with water to a thick paste, when, without application of heat, chloro-picrin distils as a colourless, uninflammable oil, of sp. gr. 1·66, boiling at 112°–113°. The vapour attacks the mucous membrane violently. Treated with iron filings and acetic acid, it yields methylamine :

$$2CCl_3(NO_2) + 12Fe + 18HO.C_2H_3O = 2CH_3.NH_2 + 4H_2O \\ + 3FeCl_2 + 9Fe(O.C_2H_3O)_2.$$

With sodic ethylate it gives ethylic ortho-carbonate (§ 227), and by heating with alcoholic ammonia, guanidine (§ 127):

$$C(NO_2)Cl_3 + 7NH_3 = C(NH)(NH_2)_2 + 3NH_4Cl + 2H_2O + N_2.$$

Dinitrodichloro-methane, $C(NO_2)_2Cl_2$, is formed by distilling naphthaline chloride with nitric acid, as a colourless oil, distillable with water vapour.

Nitro-bromoform, $CBr_3(NO_2)$, is obtained, like chloro-picrin, by heating picric acid with lime paste and bromine. It is an oil, crystalline below 10°, of sp. gr. 2·8, and possessing similar properties to chloro-picrin. It cannot be distilled under ordinary pressure without decomposition, but distils unchanged in vacuo.

Acetylic Trichloride.

543. *Acetylic trichloride*, or *trichlor ethane*, $CH_3.CCl_3$, is formed, together with ethylidene dichloride and higher substitution products, when ethylic chloride vapour is mixed with chlorine in sunlight. The reaction is generally conducted in a balloon, as in the preparation of ethylidene dichloride (fig. 21, § 473). Another still better method consists in passing chlorine on to the surface of ethylidene dichloride contained in a glass balloon exposed to sunshine. The balloon is at starting heated on a water bath until the ethylidene dichloride begins to boil. If the chlorine be added quickly, and the process:

$$CH_3.CHCl_2 + Cl_2 = HCl + CH_3.CCl_3,$$

is lively, the liquid continues to boil of itself. The action is interrupted as soon as the temperature of the boiling liquid reaches 70°. But small quantities of chlorine-richer products are then formed; there is, however, still some unaltered ethylidene dichloride. Acetylic trichloride is obtained pure by fractional distillation.

It is a colourless liquid, of chloroform-like odour, not miscible with water, boils at 73°–75°, and is converted into potassic acetate by heating with aqueous or aqueo-alcoholic potassic hydrate:

$$CH_3.CCl_3 + 4HOK = 3KCl + CH_3.CO.OK + 2H_2O.$$

Ethereal Derivatives of Acidyls,

$$C_{n'}H_{2n'+1}.C\vdots(O.C_nH_{2n+1})_3.$$

544. One molecule of an acidyl trihaloid so reacts with three molecules of a sodic alkylate that in great part the three halogen atoms are replaced by oxyalkyl groups, and the ethereal derivatives of the acidyl radicals obtained. Boiling solutions of alkaline hydrates convert these compounds into alcohols and salts of the monobasic organic acids:

$$C_{n'}H_{2n'+1}.C\vdots(O.C_nH_{2n+1})_3 + HOK + H_2O = C_{n'}H_{2n'+1}.CO.OK \\ + 3C_nH_{2n+1}.OH.$$

So far only the following compounds have been obtained:—

Formyl-triethyl ether, or *ethylic orthoformate*, $H.C\vdots(O.C_2H_5)_3$, is obtained by heating chloroform with an alcoholic solution of sodic ethylate:

$$H.CCl_3 + 3NaO.C_2H_5 = 3NaCl + H.C(O.C_2H_5)_3,$$

as a liquid boiling at 146° and insoluble in water. It yields potassic formate when heated with alcoholic potassic hydrate.

Acetyl-triethyl ether, or *ethylic ortho-acetate*, $CH_3.C\vdots(OC_2H_5)_3$, is formed by heating acetylic trichloride with sodic ethylate free from alcohol in presence of ethylic ether at 100°–120°:

$$CH_3.CCl_3 + 3NaO.C_2H_5 = 3NaCl + CH_3.C(O.C_2H_5)_3.$$

At the same time a peculiar compound is formed according to the equation:

$$CH_3.CCl_3 + 2NaO.C_2H_5 = 2NaCl + HO.C_2H_5 + CH_2:CCl(O.C_2H_5).$$

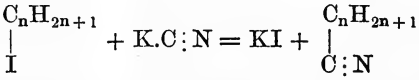
This boils at 122°, and cannot be completely separated from the acetyl-triethyl ether by fractional distillation. The latter boils at about 142°, and on heating to 120° with water decomposes into acetic acid and alcohol:

$$CH_3.C(O.C_2H_5)_3 + 2H_2O = CH_3.CO.OH + 3HO.C_2H_5.$$

Acido-nitriles, or Alkyl Cyanides, $C_{n'}H_{2n'+1}.C\vdots N$.

545. The three bonds of the acid radical can be united to a single nitrogen atom. There thereby result compounds of the true cyanogen group, $-C\equiv N$, with the alcohol radical of next lowest carbon contents, the true *alkyl cyanides, acidyl nitriles*, or *acido-nitriles*, which are isomeric with the alkyl isocyanides or alkyl carb-ammonium compounds (§§ 278 and 279).

As alkyl cyanides these compounds are obtained with carbon-nucleus synthesis when alcoholic solutions of the alkyl haloids, best the iodides, are heated with potassic cyanide or potassic mercuric cyanide:



$$\begin{matrix} C_nH_{2n+1} \\ | \\ I \end{matrix} + K.C\vdots N = KI + \begin{matrix} C_nH_{2n+1} \\ | \\ C\vdots N \end{matrix}$$

or when an intimate mixture of a potassic alkyl sulphate and potassic cyanide is submitted to dry distillation:

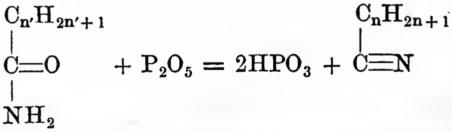
$$(C_nH_{2n+1})KSO_4 + KCN = K_2SO_4 + C_nH_{2n+1}.CN.$$

In the latter method some isocyanide, $(C_nH_{2n+1}).N\vdots C$, also distils over. In order to destroy this the distillate is shaken with water containing hydrochloric acid until the unpleasant odour of the isocyanide has disappeared; the excess of acid is neutralised by addition of dried soda, and the cyanide obtained pure on distillation.

These compounds are also formed by the action of cyanogen chloride on the zinc dialkyls:

$$2NCCl + Zn(C_nH_{2n+1})_2 = ZnCl_2 + 2N\vdots C.C_nH_{2n+1}.$$

As acido-nitriles these compounds are obtained by distillation of the acid amides with phosphoric anhydride:



$$\begin{matrix} C_{n'}H_{2n'+1} \\ | \\ C{=}O \\ | \\ NH_2 \end{matrix} + P_2O_5 = 2HPO_3 + \begin{matrix} C_nH_{2n+1} \\ | \\ C\equiv N \end{matrix}$$

546. As triad nitrogen compounds the nitriles (like prussic acid) unite directly with a molecule of a halogen hydro-acid. The compounds so formed decompose with water into an ammonic salt and free organic acid:

$$C_{n'}H_{2n'+1}.C\vdots N{<}^{H}_{Cl} + 2H_2O = NH_4Cl + C_{n'}H_{2n'+1}.CO.OH.$$

The cyanides undergo the same change when boiled with a strong mineral acid. Alkalies act on them in a similar way, giving free ammonia and the potassic salt of a monobasic acid of like carbon contents :

$$C_{n'}H_{2n'+1}.CN + HOK + H_2O = C_{n'}H_{2n'+1}.CO.OK + NH_3.$$

Nascent hydrogen converts them into the alkylamines (§ 266).

547. *Formo-nitrile,* HCN, has already been described as hydrocyanic acids amongst the cyanogen compounds (§ 74).

Aceto-nitrile, or *methylic cyanide,* $CH_3.CN$, is obtained either from methylic iodide and potassic cyanide, or best from acetamide by distillation with phosphoric anhydride. It is a colourless, agreeable-smelling liquid, which boils at 82°, mixes with water in every proportion, and burns with a violet-mantled flame.

It combines with a molecule of bromine, on heating to 100°, to a body, $CH_3.CNBr_2$, crystallising in rhombic prisms, melting and subliming at 65°, and probably of the constitution $CH_2Br.CNHBr$.

The bodies $CH_3.CN.HBr$ and $CH_3.CNHI$, obtained directly with considerable evolution of heat, are solid crystalline masses.

Aceto-nitrile also unites with phosphorous chloride, $CH_3.CN.PCl_3$, and with many metallic haloids forming crystalline compounds, such as $CH_3.CN,SbCl_5$, $(CH_3.CN)_2SnCl_4$, &c. These volatilise on heating and condense unchanged, but are decomposed by water.

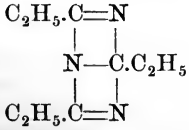
548. *Propio-nitrile,* or *ethylic cyanide,* $C_2H_5.CN$, is prepared from ethylic iodide, or ethylic potassic sulphate and potassic cyanide, also from propionamide and phosphoric anhydride. It is a colourless liquid of agreeable odour, not miscible with water in every proportion, which boils at 98° and has sp. gr. ·787. It yields similar compounds to aceto-nitrile with bromine, hydro-acids, and metallic chlorides.

If propio-nitrile be allowed to drop on metallic potassium, a violent reaction occurs, in which potassic cyanide and butane are formed :

$$2C_2H_5.CN + K_2 = 2KCN + C_4H_{10},$$

but at the same time a part polymerises to

Cyanethine, $C_9H_{15}N_3$. This latter is a white, odourless body, crystallising in leafy crystals, which melt at 190° and boil at 290° with partial decomposition. It is little soluble in cold water, is a strong base, and yields crystalline salts with one equivalent of acid, e.g. $C_9H_{15}N_3,HNO_3$. Its constitution is not yet certain, but from its formation it would appear to be *triethylic tricyanide* (§ 72) :



549. *Butyro-nitrile,* $C_3H_5.CN$, occurs as two isomerides.

1. *Propylic cyanide,* $CH_3.CH_2.CH_2.C \vdots N$, prepared from normal propylic iodide and potassic cyanide, or by distillation of butyramide and P_2O_5, is an oil boiling at 118°–119°.

2. *Isopropylic cyanide,* or *isobutyro-nitrile,* $(CH_3)_2CH.CN$, is ob-

tained from isopropylic iodide and potassic cyanide, or by long heating of isobutyric acid with potassic sulpho-cyanate :

$$(CH_3)_2CH.CO.OH + HSCN = H_2S + CO_2 + (CH_3)_2CH.CN.$$

It is an oil of peculiar aromatic odour, boiling at 107°–108°.

550. *Valero-nitriles,* or *butylic cyanides,* $C_4H_9.CN$. Four of these compounds are possible, but are not all known.

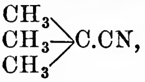
1. Normal *valero-nitrile,* or *butylic cyanide :*

$$CH_3.CH_2.CH_2.CH_2.CN,$$

is prepared from normal butylic haloids and potassic cyanide. It boils at 140·5° and has at 0° sp. gr. ·8164.

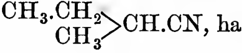
2. *Isovalero-nitrile,* or *isobutylic cyanide,* is prepared from isobutylic iodide and potassic cyanide, or by heating isovaleric acid with potassic sulpho-cyanate, as a colourless oil of bitter almond odour, of sp. gr. ·8227 at 0°, and boiling at 126°–128°.

3. *Trimethyl aceto-nitrile,* or *trimethyl carbin-cyanide :*



$$\left.\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\right> C.CN,$$

is obtained readily by the action of pure trimethyl carbin-iodide on potassic mercuric cyanide. Some isocyanide, $(CH_3)_3C.N{\equiv}C$, is always formed at the same time, but is readily decomposed by hydrochloric acid. Trimethyl aceto-nitrile is a colourless oil, boiling at 105°–106° ; on cooling it solidifies to a crystalline mass, melting at 16°.

The fourth isomeride,  $\left.\begin{matrix}CH_3.CH_2\\CH_3\end{matrix}\right> CH.CN$, has not yet been prepared.

551. *Isoamylic cyanide,* or *isocapro-nitrile :*

$$(CH_3)_2.CH.CH_2.CH_2.CN,$$

obtained by the dry distillation of isoamylic potassic sulphate with potassic cyanide, is an unpleasant-smelling oil, of boiling point 146° and sp. gr. ·806.

Dimethyl-ethyl aceto-nitrile, $C(CH_3)_2C_2H_5.CN$, boils at about 130°.

Œnantho-nitrile, or *hexyl cyanide,* $C_6H_{13}.CN$, is prepared by action of potassic cyanide on hexyl chloride.

Caprylo-nitrile, or *heptyl cyanide,* $C_7H_{15}.CN$, prepared by heating ammonic caprylate with phosphoric anhydride, boils at 194°–196° and has sp. gr. ·8201 at 13·3°.

Pelargo-nitrile, or *octylic cyanide,* $C_8H_{17}.CN$, prepared by boiling octylic cyanide with potassic iodide and alcohol, boils at 206° and has sp. gr. ·8187 at 14°.

Cetylic cyanide, or *margaro-nitrile,* $C_{16}H_{31}.CN$, is prepared by the action of cetylic iodide upon potassic cyanide, though not in a completely pure condition.

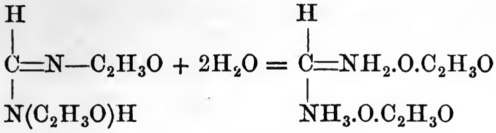
Acidyl Diamines, $C_{n'}H_{2n'+1}.C\begin{matrix}\diagup NH_2\\ = NH\end{matrix}$

552. Of the compounds of the acid radicals with two nitrogen atoms—one amide and one imide group—only the members poorest in carbon are known, and then only in compounds with acids.

553. *Formyl diamine,* or *formyl imide-amide,* CH_4N_2, or $CH(NH)NH_2$. On heating formyl triethylate with acetamide to 180° both bodies react according to the equation:

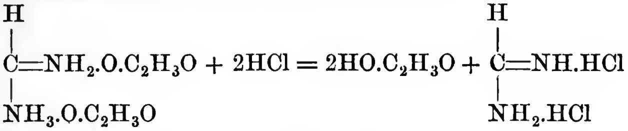
$$CH(O.C_2H_5)_3 + 2N(C_2H_3O)H_2 = 3HO.C_2H_5 + CH\left\{\begin{matrix}=N.(C_2H_3O)\\ -N(C_2H_3O)H\end{matrix}\right.$$

This *diacetyl-formyl diamine* crystallises in colourless cubes, which on heating with water yield formyl diamine acetate:



$$\begin{array}{l}H\\ |\\ C{=}N{-}C_2H_3O\\ |\\ N(C_2H_3O)H\end{array} + 2H_2O = \begin{array}{l}H\\ |\\ C{=}NH_2.O.C_2H_3O\\ |\\ NH_3.O.C_2H_3O\end{array}$$

This on evaporation with hydrochloric acid gives:

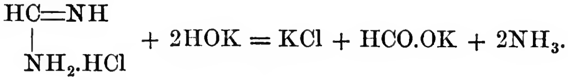


$$\begin{array}{l}H\\ |\\ C{=}NH_2.O.C_2H_3O\\ |\\ NH_3.O.C_2H_3O\end{array} + 2HCl = 2HO.C_2H_3O + \begin{array}{l}H\\ |\\ C{=}NH.HCl\\ |\\ NH_2.HCl\end{array}$$

which yields with platinic chloride golden yellow crystals of the double salt $CH_4N_2,2HClPtCl_4$. On heating prussic acid hydrochloride (§ 77) with absolute alcohol, the mono-hydrochloride of formyl diamine is obtained:

$$2CH\vdots NHCl + 2C_2H_5.OH = C_2H_5Cl + CHO.O.C_2H_5 + CH(NH).NH_2.HCl,$$

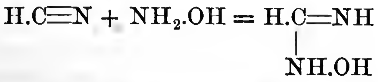
forming colourless crystals melting at 81°; and on addition of alkali yielding ammonia and a formate:



$$\begin{array}{l}HC{=}NH\\ |\\ NH_2.HCl\end{array} + 2HOK = KCl + HCO.OK + 2NH_3.$$

A related body is isomeric with urea, namely:

Isuret, formyl-imid hydroxylamide, $CH(NH).NH.OH$. It is formed by the direct union of prussic acid with hydroxylamine in alcoholic solution:



$$H.C{\equiv}N + NH_2.OH = \begin{array}{l}H.C{=}NH\\ \quad|\\ \quad NH.OH\end{array}$$

It crystallises in rhombic prisms, which are readily soluble in water, difficultly in alcohol, and melt at 104°–105°. The aqueous solution on boiling decomposes in very complicated manner, urea, biuret, guanidine, ammonia, carbonic acid, and nitrogen being formed.

554. *Acetyl diamine,* or *acediamine:*

$$C_2H_6N_2 \text{ or } CH_3.C\left\{\begin{matrix}-NH_2\\ =NH\end{matrix}\right.$$

is obtained as hydrochloride, together with ammonic chloride, diacetamide, and free acetic acid, on heating acetamide in a stream of dry hydrochloric acid gas :

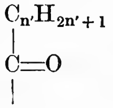
$$2CH_3.CO.NH_2 + HCl = CH_3.CO.OH + CH_3.C \vdots (NH)(NH_2.HCl).$$

On distillation the salt remains in white needles, which can be recrystallised from ether alcohol. With platinic chloride it yields the crystalline double salt $[CH_3.C(NH)(NH_2)HCl]_2,PtCl_4$. By mixing a solution of the hydrochloride with solutions of argentic salts, other salts, containing one equivalent of acid, can be prepared. On endeavouring to obtain the free base from these, it decomposes into ammonia and ammonic acetate :

$$CH_3.C(NH)(NH_2) + 2H_2O = NH_3 + CH_3.CO.O.NH_4.$$

DERIVATIVES OF THE ACIDOXYLS, $C_{n'}H_{2n'+1}.CO$.

555. By combination of an acid radical with the two bonds of an oxygen atom, there result the very stable monad *acidoxyls* or *oxy-radicals :*

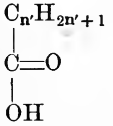


$$\begin{array}{c} C_{n'}H_{2n'+1} \\ | \\ C{=}O \\ | \end{array}$$

of the monobasic organic so-called *fatty acids :*

$$C_nH_{2n}O_2 = C_{n'}H_{2n'+1}.CO.OH,$$

or



$$\begin{array}{c} C_{n'}H_{2n'+1} \\ | \\ C{=}O \\ | \\ OH \end{array}$$

By action of various chemical bodies on the acids the acidoxyls behave in many ways like the alcohol radicals. The hydroxyl group is replaced by halogen when they are treated with phosphoric haloids, the halogen compounds of the *acidoxyls* being produced :

$$C_{n'}H_{2n'+1}.CO.Cl\,;$$

on replacing the hydroxyl by amidogen, NH_2, the acidoxyl amides, $C_{n'}H_{2n'+1}.CO.NH_2$, are formed ; and the diacidoxyl amides :

$$(C_{n'}H_{2n'+1}.CO)_2NH,$$

and triacidoxyl amides, $(C_nH_{2n+1}.CO)_3N$, stand in very close relation to these latter.

If the hydroxylic oxygen atom of an organic acid be replaced by sulphur, the compounds formed, the *acidoxyl sulph-hydrates,* possess the character of monobasic acids, and are termed *thio-acids,* $C_{n'}H_{2n'+1}.CO.SH$.

The hydrogen atoms in the groups OH and SH united to acidoxyls are distinguished by the ease with which they are replaced by basic metals or by alcohol radicals, salts of the fatty acids being thereby formed :

$$\begin{array}{ll} C_{n'}H_{2n'+1}.CO.OM & C_{n'}H_{2n'+1}.CO.O.C_{n''}H_{2n''+1} \\ C_{n'}H_{2n'+1}.CO.SM & C_{n'}H_{2n'+1}.CO.S.C_{n''}H_{2n''+1} \end{array}$$

If the respective hydrogen atoms be replaced by acidoxyl groups, the *diacidoxyl oxides* or *acid anhydrides*, $C_{n'}H_{2n'+1}.CO.O.CO.C_{n''}H_{2n''+1}$, and the *diacidoxyl sulphides* or *sulph-anhydrides* :

$$C_{n'}H_{2n'+1}.CO.S.CO.C_{n''}H_{2n''+1},$$

are obtained.

The *aldehydes* (§ 383), $C_nH_{2n+1}.CO.H$, may be considered as the hydrides of the acidoxyls, standing to the acids in the same relations as those of the paraffins to the alcohols of the series $C_nH_{2n+1}.OH$. The *ketones* may be looked on—in agreement with several of their methods of formation (§ 436)—as compounds of the acidoxyls with alcohol radicals :

$$CH_3.CO.CH_3, \text{ acetone} = \text{acetyl-methyl}.$$

As the acids occur frequently in nature in the free state or in form of their metallic or ethereal salts—in the latter case mostly as salts of the trihydric alcohol glycerine, forming the chief constituents of animal and vegetable fats—it is advisable to consider them before all other acidoxyl compounds, which are generally prepared from them.

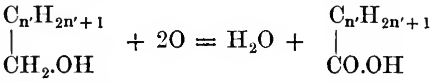
The Monobasic Fatty Acids, $C_nH_{2n}O_2$.

Acidoxyl Hydrates, $C_nH_{2n-1}O.OH$ or $C_{n'}H_{2n'+1}.CO.OH$.

556. The homologous series of fatty acids contains members with from one to thirty carbon atoms.

In the case of the three first members, as in that of the primary alcohols of like carbon contents, no isomers exist, but the formula $C_4H_7O.OH$ corresponds to two isomeric acids, which are obtained by oxidation of the two primary butylic alcohols (§ 169). With increase in the carbon contents the number of possible isomers increases in rapid progression.

In general the number of possible acids of any given carbon contents is the same as that of the primary alcohols, with like number of carbon atoms, as only primary alcohols can be converted into acids by oxidation without alteration of the carbon nucleus :



$$\begin{array}{l}C_{n'}H_{2n'+1}\\ |\\ CH_2.OH\end{array} + 2O = H_2O + \begin{array}{l}C_{n'}H_{2n'+1}\\ |\\ CO.OH\end{array}$$

Further, as the number of primary alcohols of equal number of carbon atoms, *n*, is as great as that of all—primary, secondary, and tertiary—alcohols of the next lowest number of carbon atoms, $n - 1$, the number of possible isomeric acids with *n* carbon atoms must also be the same, as every fatty acid is the compound of the next lowest alkyl, $C_{n-1}H_{2(n-1)+1}$ or $C_{n'}H_{2n'+1}$, if $_{n-1}={}_{n'}$, with the *carboxyl hydrate group*, CO.OH.

Above C_{18} many members entirely lack representatives; the number of known members of the series is, however, larger than in the alcohols, $C_nH_{2n+1}.OH$.

With increasing carbon contents the solubility of the fatty acids rapidly diminishes, and the melting and boiling points rise, with the modifications already mentioned (§§ 54–57). Acids containing more than ten carbon atoms in the nucleus can no longer be volatilised unchanged under ordinary atmospheric pressure, but suffer dry distillation on heating; under reduced pressure the limit of unaltered volatilisation is higher, and, though not yet determined, certainly above a nucleus of eighteen carbon atoms (comp. § 594).

557. The following is a table of the general composition of the known members of the series :—

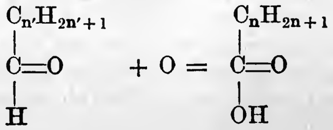
Formic acid	CH_2O_2	$= H.CO.OH$	(hydro-carbonic acid)
Acetic acid	$C_2H_4O_2$	$= CH_3.CO.OH$	(methyl carbonic acid)
Propionic acid	$C_3H_6O_2$	$= C_2H_5.CO.OH$	(ethyl carbonic acid)
Butyric acids	$C_4H_8O_2$	$= C_3H_7.CO.OH$	(propyl carbonic acids)
Valeric acids	$C_5H_{10}O_2$	$= C_4H_9.CO.OH$	(butyl carbonic acids)
Caproic acids	$C_6H_{12}O_2$	$= C_5H_{11}.CO.OH$	(amyl carbonic acids)
Œnanthylic acids	$C_7H_{14}O_2$	$= C_6H_{13}.CO.OH$	(hexyl carbonic acids)
Caprylic acids	$C_8H_{16}O_2$	$= C_7H_{15}.CO.OH$	(heptyl carbonic acids)
Pelargonic acid	$C_9H_{18}O_2$	$= C_8H_{17}.CO.OH$	(octyl carbonic acid)
Capric acid	$C_{10}H_{20}O_2$	$= C_9H_{19}.CO.OH$	
Undecylic acid	$C_{11}H_{22}O_2$	$= C_{10}H_{21}.CO.OH$	
Lauric acid	$C_{12}H_{24}O_2$	$= C_{11}H_{23}.CO.OH$	
Tridecylic acid	$C_{13}H_{26}O_2$	$= C_{12}H_{25}.CO.OH$	
Myristic acid	$C_{14}H_{28}O_2$	$= C_{13}H_{27}.CO.OH$	
Pentadecylic acid	$C_{15}H_{30}O_2$	$= C_{14}H_{29}.CO.OH$	
Palmitic acids	$C_{16}H_{32}O_2$	$= C_{15}H_{31}.CO.OH$	
Margaric acid	$C_{17}H_{34}O_2$	$= C_{16}H_{33}.CO.OH$	
Stearic acid	$C_{18}H_{36}O_2$	$= C_{17}H_{35}.CO.OH$	
—	—	—	
Arachidic acid	$C_{20}H_{40}O_2$	&c.	
—	—		
Behenic acid	$C_{22}H_{44}O_2$		
—	—		
—	—		
Hyaenic acid	$C_{25}H_{50}O_2$		
—	—		
Cerotic acid	$C_{27}H_{54}O_2$		
—	—		
—	—		
Mellissic acid	$C_{30}H_{60}O_2$		

Preparation of Fatty Acids.

558. The fatty acids can be obtained *without essential alteration of the carbon nucleus* of the bodies they are prepared from, and especially without alteration of the number of carbon atoms—

1. From the *primary alcohols*, $C_nH_{2n+1}.OH$, their ethers, and other oxy compounds of the alkyls, by oxidation with ozone or oxidising agents or by fused potassic hydrate (§§ 160, 1, and 556).

2. From the *aldehydes*, $C_nH_{2n}O$, which are themselves obtained from the primary alcohols by less active oxidation :



$$\begin{matrix} C_{n'}H_{2n'+1} \\ | \\ C{=}O \\ | \\ H \end{matrix} + O = \begin{matrix} C_nH_{2n+1} \\ | \\ C{=}O \\ | \\ OH \end{matrix}$$

The oxidising agent employed for the alcohols is a mixture of potassic bichromate and sulphuric acid, the reaction generally starting without external application of heat:

$$3C_{n'}H_{2n'+1}.CH_2.OH + 2K_2Cr_2O_7 + 8H_2SO_4 = 2K_2Cr_2(SO_4)_4 \\ + 11H_2O + 3C_{n'}H_{2n'+1}.CO.OH$$

3. The acido-nitriles (§ 546) are converted into the free fatty acids by heating with aqueous hydrochloric or sulphuric acids:

$$C_{n'}H_{2n'+1}.CN + HCl + 2HOH = NH_4Cl + C_{n'}H_{2n'+1}.CO.OH;$$

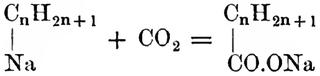
and on boiling with solution of potassic hydrate they yield ammonia and the potassic salt of the fatty acid:

$$C_{n'}H_{2n'+1}.CN + H_2O + HOK = NH_3 + C_nH_{2n+1}.CO.OK.$$

559. The fatty acids can be obtained, with *increase* of the carbon nucleus, by several methods from the alcohols of next lower number of carbon atoms. Of these methods there may be mentioned—

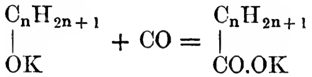
1. From the alcohols, by means of their haloids or hydric sulphates, the alkyl cyanides or acido-nitriles are prepared, and these then transformed as above.

2. Mixtures of sodium alkyls with zinc dialkyls (§ 371) absorb dry carbonic anhydride, which unites with the sodium compound, forming a sodium salt of the alkyl carbonic acid:



$$\begin{array}{l} C_nH_{2n+1} \\ | \\ Na \end{array} + CO_2 = \begin{array}{l} C_nH_{2n+1} \\ | \\ CO.ONa \end{array}$$

3. Alcoholic solutions of potassic alkylates (§ 197) slowly absorb dry carbon monoxide gas on warming, and yield, though with difficulty, the potassic salts of the alkyl carbonic acids:



$$\begin{array}{l} C_nH_{2n+1} \\ | \\ OK \end{array} + CO = \begin{array}{l} C_nH_{2n+1} \\ | \\ CO.OK \end{array}$$

A better result is obtained by the use of dry sodic alkylates and higher temperatures (190°–210°), but the reaction appears to be confined to the lower members of the series, taking an entirely different course with sodic isoamylate.

4. A method of very general application in the synthesis of fatty acids starts from the product of the action of sodium upon ethylic acetate (see this). The ethylic aceto-acetate, separable therefrom, dissolves an atom of sodium with evolution of hydrogen, and yields pure ethylic sodaceto-acetate, $CH_3.CO.CHNa.CO.O.C_2H_5$, in which, by action of alkyl haloids, the sodium atom can be replaced by an alkyl group. The ethylic alkyl aceto-acetates:

$$\left.\begin{array}{l} CH_3.CO \\ C_nH_{2n+1} \end{array}\right\} CH.CO.O.C_2H_5,$$

so obtained (which, by boiling with alkalies, yield ketones [§ 436, 2]), on heating alone, or better with ethylic sodaceto-acetate or sodic ethylate, eliminate $CH_2.CO$ (of which several groups coalesce to form complicated molecules, e.g. dehydracetic acid) and give the ethylic salt of a fatty acid :

$$\left.\begin{array}{l}CH_3.CO\\ C_nH_{2n+1}\end{array}\right\}CH.CO.O.C_2H_5 = C_2H_2O + C_{n'}H_{2n'+1}.CH_2.CO.O.C_2H_5,$$

from which the synthetically formed fatty acid is obtained on saponification.

The ethylic alkyl aceto-acetates can further exchange an atom of hydrogen for sodium. The ethylic alkyl sodaceto-acetates :

$$\left.\begin{array}{l}CH_3.CO\\ C_{n'}H_{2n'+1}\end{array}\right\}CNa.CO.O.C_2H_5,$$

thus formed, yield, on heating with alkyl iodides, sodic iodide and an ethylic dialkyl aceto-acetate :

$$\left.\begin{array}{r}CH_3.CO\\ C_{n'}H_{2n'+1}\\ Na\end{array}\right\}C.CO.O.C_2H_5 + IC_{n''}H_{2n''+1} = NaI$$
$$+ \left.\begin{array}{l}CH_3CO\\ C_{n'}H_{2n'+1}\\ C_{n''}H_{2n''+1}\end{array}\right\}C.CO.O.C_2H_5,$$

from which, by similarly conducted elimination of the group C_2H_2O, the ethylic salt of a new fatty acid results, which contains a secondary alcohol radical united with CO.OH :

$$\left.\begin{array}{l}CH_3.CO\\ C_{n'}H_{2n'+1}\\ C_{n''}H_{2n''+1}\end{array}\right\}C.CO.OC_2H_5 = C_2H_2O$$
$$+ \left.\begin{array}{l}C_{n'}H_{2n'+1}\\ C_{n''}H_{2n''+1}\end{array}\right\}CH.CO.O.C_2H_5.$$

560. Fatty acids are obtained with *splitting*, i.e. diminution of the carbon nucleus by numerous decompositions of carbon-richer compounds. As already mentioned, the *secondary alcohols* and their first oxidation products, the *ketones*, yield by the action of powerful oxidising agents (chromic and sulphuric acids on heating) always at least two molecules of acid, the sum of whose carbon atoms is the same as the number of carbon atoms in the parent body (§ 437). *Tertiary alcohols* on oxidation are generally decomposed into three or more acid molecules.

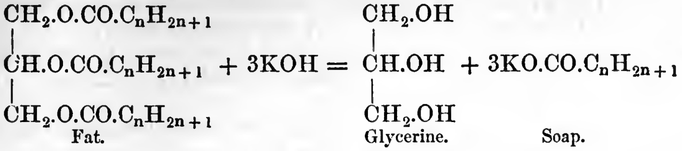
As general methods there may be mentioned the splitting up of the acids of the *lactic series* by heating with sulphuric acid or oxidation, or that of the acids of the acrylic series by fusion with potassic hydrate.

561. Very important methods of obtaining fatty acids start from their naturally occurring alcoholic salts, especially from the vegetable and animal fats. These, on heating with aqueous or alcoholic solutions of strong basic hydrates, yield the respective alcohols together with a metallic salt of the fatty acid :

$$C_{n''}H_{2n''+1}.O.CO.C_{n'}H_{2n'+1} + KOH = C_{n''}H_{2n''+1}.OH$$
$$+ KO.CO.C_{n'}H_{2n'+1}.$$

The alkali salts of monobasic fatty acids of high molecular weight, which dissolve unchanged in alcohol and little water, but are partially decomposed by much water into free alkali and fatty acid (which latter causes the liquid to appear turbid, and to froth strongly on shaking), are termed *soaps*, and from this the process of decomposition of all alcoholic salts by alkalies has been termed '*saponification*.'

The *fats* are organic salts of the trihydric alcohol glycerine, and yield therefore, on saponification, glycerine and three molecules of the alkali salt of an organic acid :



$$\begin{array}{llll} CH_2.O.CO.C_nH_{2n+1} & & CH_2.OH & \\ | & & | & \\ CH.O.CO.C_nH_{2n+1} & + 3KOH = & CH.OH & + 3KO.CO.C_nH_{2n+1} \\ | & & | & \\ CH_2.O.CO.C_nH_{2n+1} & & CH_2.OH & \\ \text{Fat.} & & \text{Glycerine.} & \text{Soap.} \end{array}$$

Most of the natural fats contain the glycerine salts of several fatty acids, most also of acids of the oleic series, $C_nH_{2n-3}O.OH$, and therefore yield on saponification a mixture of potassic salts, from which mineral acids set free a mixture of acids. The separation of the single acids is in such cases attended with extraordinary difficulties, and is partly impossible even.

If together with non-volatile acids of high molecular weight also acids of lower molecular weight, which can be volatilised unchanged, occur, the two groups can be separated by distillation with water vapour. The distillate then contains the volatile acids, either dissolved in the water or floating as an oily layer on its surface. In order to separate them further, as a rule they are converted into baric salts by boiling with solution of baric hydrate, and these—utilising the different solubility of the respective salts—separated from one another by crystallisation, each one being purified by repeated recrystallisation.

562. If only two volatile acids have to be separated from one another, this can be effected either by fractional distillation, or the *method of partial saturation* with following distillation may be used. One half of the acid mixture is neutralised with alkali, the other half then added, and the whole aqueous solution submitted to distillation as long as any liquid of acid reaction passes over. The distillate then contains mainly the acid of lower boiling point, with a small quantity of the less volatile acid, the residue mainly of a salt of the latter. By renewed partial saturation and distillation, and if needful frequent repetition of the process on the distillate, the non-volatile acid is at last obtained alone in aqueous solution, but evidently with great loss in the process. From the residue of the first distillation, containing a little of the salt of the more volatile and much of the salt of the less volatile acid, the latter is obtained pure by decomposing the salts with sulphuric acid, distilling, half saturating the distillate, and again distilling. The residual salt is again subjected to a similar process, until at last the less volatile acid salt is left in a state of purity.

563. From mixtures of non-volatile acids the admixed members of the oleic series must first be removed. This is effected by precipitating the solution of the alkali salts by plumbic acetate, and so converting them into the insoluble lead salts (lead plaster); this latter is then dried and extracted with ether as long as any lead salts of oleic acids are removed. By evaporating the ether from this solution the lead salts of the oleic acids are obtained, from which the latter can be separated.

The portion insoluble in ether consists of the lead salts of the acids of the fatty series rich in carbon, which can be liberated by decomposition with mineral acids, especially hydrochloric acid.

The preparation of the pure acids is attended with great difficulties and loss, as with not too great difference in composition there is but little difference in properties. If the mixture contains but two members of the series (e.g. palmitic and stearic acids), the partial separation succeeds only by the method of *partial precipitation*. The mixture is dissolved in alcohol, and alcoholic solution of magnesic acetate added with constant stirring in such quantity that only about one-seventh of the fatty acids shall be precipitated as magnesic salt, and the precipitate *a* then separated from the solution *b* of the greatest part of the acid mixture by filtration. *a* consists mainly of the magnesic salt of the acid richer in carbon (stearic acid), but is still contaminated by the acid poorer in carbon. It is therefore decomposed by hydrochloric acid, the free fatty acid dissolved again in alcohol, and one-seventh precipitated by magnesic acetate. This precipitate, which contains only $\frac{1}{49}$ of the quantity of the original mixture of acids, consists nearly entirely of the salt of the acid richer in carbon, but as a rule requires further treatment in a similar manner, in order to obtain it in a state of chemical purity. This point is settled by means of the melting point.

The filtrate *b* from the first precipitation is now partly precipitated by slow addition of magnesic acetate, whereby the later precipitates, and still more the solution, become richer and richer in the acid, poorer in carbon (palmitic acid), until at last—the successive additions of magnesic salt being always smaller—a solution is obtained which contains the latter acid only.

564. That the fatty acids can be converted into members of the foregoing series has been already mentioned at the respective places; it will therefore suffice to merely recapitulate.

Conversion of fatty acids into *paraffins*—

1. Without increase and with diminution of the carbon nucleus (§ 149).
2. With formation of larger carbon nuclei by electrolysis of the fatty alkaline salts (§ 150).

Conversion into aldehydes (§ 386), and through these into the corresponding primary alcohols (§ 388).

Conversion into *ketones* richer in carbon by dry distillation of the salts (§ 435), and through the ketones into secondary alcohols (§ 434).

Conversion into tertiary alcohols by means of the acid chlorides (§ 163).

565. By oxidation of acids richer in carbon, by distillation with manganic dioxide and sulphuric acid, there are formed, together with carbonic anhydride and water, salts of the unchanged acids with alcohols of less carbon contents. Butyric acid, for instance, yields propylic butyrate:

$$CH_3.CH_2.CH_2.CO.OH + HO.CO.CH_2.CH_2.CH_3 + O$$
$$= CH_3.CH_2.CH_2.CO.O.CH_2.CH_2.CH_3 + CO_2 + OH_2.$$

566. If pure fatty acids, soluble in water, be brought into contact with water, there occurs—frequently with considerable evolution of heat—a diminution of the total volume, which appears to be greatest when one molecule of acid is mixed with one molecule of water. The product thereby formed is the *acidyl trihydrate:*

$$C_{n'}H_{2n'+1}.C\genfrac{}{}{0pt}{}{:O}{.OH} + H_2O = C_{n'}H_{2n'+1}C\left\{\begin{matrix}OH\\OH\\OH\end{matrix}\right.$$

corresponding to the acidyl ethers (§ 544). These compounds, similarly to the dihydrates of the aldehyde radicals (§ 383), are but little stable, and on distillation partly decompose into their components. If brought together with bases they yield the salts of the monobasic fatty acids:

$$C_{n'}H_{2n'+1}.C(OH)_3 + KOH = C_{n'}H_{2n'+1}.CO.OK + 2H_2O,$$

which generally are left anhydrous on drying at 100°.

The anhydrous fatty acids are attacked by chlorine and bromine, especially on heating and exposure to sunlight, with formation of halogen substitution acids. The first replacement by a halogen atom occurs in general in the α position, i.e. on that carbon atom which is united to carboxyl hydrate:

$$CH_3.CH_2.CO.OH + Cl_2 = HCl + CH_3.CHCl.CO.OH$$

α-Chlor-propionic acid.

$$CH_3.CH_2.CH_2.CO.OH + Br_2 = HBr + CH_3.CH_2.CHBr.CO.OH$$

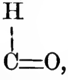
α-Brom-butyric acid.

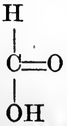
$$(CH_3)_2.CH.CO.OH + Br_2 = HBr + (CH_3)_2:CBr.CO.OH$$

α-Brom-isobutyric acid.

In these substitution bodies, by boiling with alkalies, the halogen atom can be replaced by hydroxyl, so yielding the α-oxyacids of the lactic series.

Formic Acid, CH_2O_2.

567. *Formic acid*, *formoxyl hydrate*, HCO.OH, occurs ready-formed in ants, stinging nettles, pine needles, &c., from which it can be separated by distillation with water. Although it is the first member of the series of fatty acids, it differs in one essential from all others, inasmuch as in it the carboxyl-hydrate group is united not with an alcohol radical, but with hydrogen. As *hydro-carbonic acid*, or compound of the aldehyde group,  $\begin{array}{l}H\\ |\\ C{=}O\end{array}$, with hydroxyl:



$$\begin{array}{l}H\\ |\\ C{=}O\\ |\\ OH\end{array}$$

it is the half-aldehyde of carbonic acid, and is converted into the latter by the action of oxidising agents:

$$H.CO.OH + O = HO.CO.OH = H_2O + CO_2.$$

In agreement with this view it can be prepared from carbonic anhydride by the action of nascent hydrogen in the presence of alkaline hydrates. Potassium is placed in a dry basin floating on luke-warm water, covered with a bell filled with carbonic anhydride, and left to itself for 24 hours, when the metal is found to be converted into a mixture of potassic carbonate :

$$K_2 + CO_2 + H_2O = K_2CO_3 + 2H,$$

and potassic formate :

$$K_2 + 2CO_2 + 2H = 2H.CO.OK.$$

Some formate is also formed in a similar reaction in the decomposition of sodium amalgam by a concentrated aqueous solution of ammonic carbonate :

$$CO(ONH_4)_2 + 2Na = H.CO.ONa + NaOH + 2NH_3,$$

and by boiling a mixture of powdered zinc and zincic carbonate with solution of potassic hydrate :

$$ZnCO_3 + Zn + 5KOH = 2Zn(OK)_2 + HCO.OK + 2H_2O.$$

Carbonic oxide is slowly absorbed at 100° by the most concentrated solution of potassic hydrate, with formation of potassic formate :

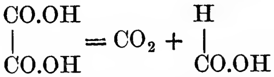
$$CO + HOK = HCO.OK.$$

It is formed from hydrocyanic acid, formo-nitrile, by decomposition with water, usually assisted by the presence of mineral acids (§ 76) or alkalies (§ 79), and from methylic alcohol by ozone or heated soda lime (§ 165).

The formyl trihaloids (chloroform, &c.) and formyl triethylate yield formate on heating with alcoholic potassic hydrate (§§ 538 and 544).

Formic acid is of frequent occurrence as an oxidation product of other organic bodies of higher molecular weight, as ketones containing methyl, many acids of the lactic series, malic, tartaric, and citric acids, the sugars and their congeners. Formerly it was generally prepared by the distillation of sugar or starch with sulphuric acid and manganic dioxide or potassic chromate.

It is now usually prepared from oxalic acid. This on heating alone yields some formic acid :



$$\begin{array}{l} CO.OH \\ | \\ CO.OH \end{array} = CO_2 + \begin{array}{l} H \\ | \\ CO.OH \end{array}$$

A very good yield is obtained when crystallised oxalic acid is added to glycerine, rendered as free as possible from water, and heated to 100°–110°. Evolution of carbonic anhydride commences, and at the same time very dilute formic acid distils. The greater part reacts with the glycerine, forming monoformin, or glycerine monoformate :

$$C_3H_5(OH)_3 + [C_2O_2(OH)_2,2H_2O] = C_3H_5(OH)_2(O.CHO) + CO_2 + 3H_2O.$$

As soon as the evolution of carbonic anhydride ceases, and without alteration of the temperature, a new quantity of oxalic acid is added, whose water of crystallisation is partly evolved and partly resolves the monoformin into glycerine and formic acid:

$$C_3H_5(OH)_2(O.CHO) + H_2O = C_3H_5(OH)_3 + HO.CHO.$$

The dried oxalic acid converts anew unaltered glycerine into the monoformate until the liquid becomes rich in this latter; the formation exceeds the decomposition, but the amount of the latter continually increases, so that formic acid of increasing concentration distils over. At last, with continued addition of crystallised oxalic acid, the formation and decomposition of the monoformin reach an equal amount, and a distillate passes over containing 56 % of formic acid and 44 % of water.

By careful heating of glycerine with anhydrous oxalic acid, a solution of formic acid of 70 % may be obtained (formyl trihydrate).

All the methods described, as also distillation of formates with dilute sulphuric acid, yield aqueous formic acid. In order to obtain it anhydrous, the dry lead salt is decomposed by dry sulphuretted hydrogen at a temperature not exceeding 100°, when anhydrous formic acid distils:

$$Pb(O.CHO)_2 + H_2S = PbS + 2HO.CHO,$$

which is freed from any absorbed sulphuretted hydrogen by repeated rectification over plumbic formate. A 70 % formic acid solution can also be deprived of its water by addition of dried oxalic acid, with gentle heating. On cooling, crystallised oxalic acid separates, and the decanted liquid yields anhydrous formic acid on distillation.

568. Pure formic acid is a colourless, mobile liquid, which solidifies to a crystalline mass below 0°, melts at 8·5°, and boils at 99°. Its sp. gr. is 1·233. It has a penetrating acid odour, and raises blisters on the skin. It unites with a molecule of water (71·9 pts. $CH_2.O_2$ and 28·1 H_2O) to form formyl trihydrate:

$$HCO.OH + H_2O = HC(OH)_3,$$

a liquid which does not solidify at −15° and which boils at 106°.

Concentrated sulphuric acid decomposes formic acid, with brisk evolution of carbonic oxide:

$$H.CO.OH + H_2SO_4 = CO + H_4SO_5.$$

Chlorine and oxidising agents decompose it with formation of carbonic anhydride:

$$\begin{aligned} H.CO.OH + Cl_2 &= CO_2 + 2HCl \\ H.CO.OH + O \ &= CO_2 + H_2O. \end{aligned}$$

The oxides of the noble metals are thereby reduced to metal:

$$\begin{aligned} CH_2O_2 + HgO \ &= CO_2 + H_2O + Hg \\ CH_2O_2 + Ag_2O &= CO_2 + H_2O + Ag_2. \end{aligned}$$

569. *Formates* are all soluble in water, and generally crystallise well. They are obtained by the solution of metallic oxides, hydrates, or carbonates in aqueous formic acid.

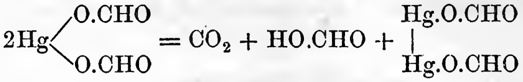
Ammonic formate, $(NH_4)O.CHO$, crystallises in very readily soluble rectangular prisms. On heating to 180° it decomposes into water and hydrocyanic acid (comp. § 76):

$$H.CO.O.NH_4 = 2H_2O + HCN.$$

Plumbic formate, $Pb(O.CHO)_2$, forms characteristic long, brilliant needles, rather difficultly soluble.

Cupric formate, $Cu(O.CHO)_2,4H_2O$, forms large blue, transparent crystals.

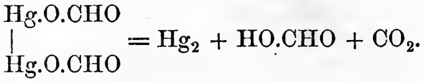
On shaking aqueous formic acid with mercuric oxide, the latter dissolves in large quantity to *mercuric formate*. The clear solution now begins to cloud, more quickly on warming, evolves carbonic anhydride, and deposits difficultly soluble, silky crystals of the mercurous salt:



$$2Hg\begin{cases}O.CHO\\O.CHO\end{cases} = CO_2 + HO.CHO + \begin{array}{l}Hg.O.CHO\\ \mid \\Hg.O.CHO\end{array}$$

Mercurous formate.

which soon further decompose into formic acid, carbonic anhydride, and mercury:



$$\begin{array}{l}Hg.O.CHO\\ \mid \\Hg.O.CHO\end{array} = Hg_2 + HO.CHO + CO_2.$$

If argentic nitrate be mixed with a not too dilute solution of an alkaline formate, white crystals of *argentic formate* precipitate, which very soon blacken and decompose:

$$2AgO.CHO = Ag_2 + HO.CHO + CO_2.$$

Acetic Acid, $C_2H_4O_2$.

570. *Acetic acid, acetyl hydrate*, $HO.C_2H_3O$, or *methyl-carbonic acid*, $CH_3.CO.OH$, is the oldest known acid. It occurs frequently in small quantities, in form of salts, in vegetable and animal fluids, and is obtained in the decay of many organic bodies. It occurs largely as an oxidation product of organic bodies, whether the oxidation be effected in the wet way (e.g. from lactic acid) or by fusion with alkaline hydrates (e.g. malic acid). It is also formed by the dry distillation of complicated compounds, such as wood, starch, &c.

Sodium methyl is converted by absorption of carbonic anhydride into sodic acetate:

$$CH_3.Na + CO_2 = CH_3.CO.ONa.$$

Aceto-nitrile, or methylic cyanide, yields the same salt on boiling with sodic hydrate solution:

$$CH_3.CN + H_2O + HONa = CH_3.CO.ONa + NH_3,$$

or free acetic acid when heated with hydrochloric acid:

$$CH_3.CN + 2H_2O + HCl = NH_4Cl + CH_3.CO.OH.$$

Technically, acetic acid is prepared from ethylic alcohol, or from the products of the dry distillation of wood.

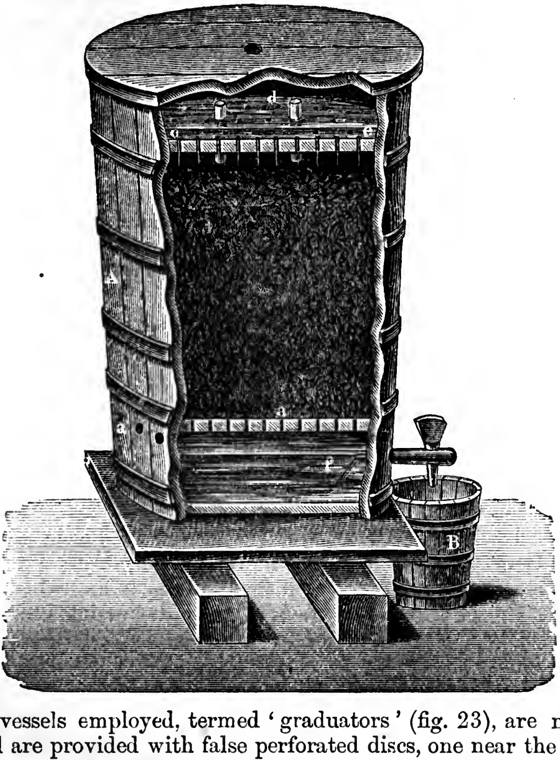
Dilute alcoholic liquids, especially such as contain other animal or vegetable bodies capable of decomposition, and mineral salts (beer, light wines), as also impure sugar solutions (juice of fruits, wort, honey-water), become acid on standing in the air, especially at temperatures between 20° and 40°, acetic acid being formed (vinegar).

The cause of this change is always an organised ferment, which has the power of absorbing the atmospheric oxygen and carrying it to oxidised bodies. As this ferment is contained in large quantity in crude vinegar, some of this is always added to the alcoholic or saccharine liquid, in order to start the fermentation more quickly.

Platinum black acts similarly to this organised ferment, and in presence of air converts concentrated alcohol into pretty concentrated acetic acid, heat being evolved.

571. Aqueous acetic acid is generally prepared on the large scale by the process known as 'quick vinegar process.'

Fig. 23.



The vessels employed, termed 'graduators' (fig. 23), are made of oak, and are provided with false perforated discs, one near the bottom of the vessel and again near the top. The space between these is filled with shavings, whilst the perforations in the upper disc are loosely filled with pieces of string. The shavings are first moistened with vinegar, in order to sow the ferment; there is then poured on the upper disc a dilute brandy (of 10–12 % alcohol), which slowly passes through the capillaries of the strings on to the shavings, and flowing over these exposes a very considerable surface to the air. Care must then be taken that a stream of air sufficient for the oxidation of the alcohol shall pass through the interior of the vessel. This is effected by holes *a* in the sides of the vessel, whilst the warm residual air (nitrogen) escapes through the upper openings *d* and *e*. Dilute vinegar collects at the bottom of the flask, and is drawn off by a tap. The product contains, as a rule, unaltered alcohol, for whose complete conversion the liquid is passed once or twice more through the apparatus.

The regulation of the amount of air is of great importance. If there be not enough, much aldehyde volatilises, whilst, if the air stream be too quick, the temperature in the interior of the apparatus never reaches the necessary height.

A large portion of the acetic acid employed for industrial purposes is obtained from the aqueous products of the distillation of wood (comp. § 165). From this, by saturation with lime, calcic acetate is prepared, which remains behind in solution on the distillation of the methyl-alcohol, acetone, &c. The cleared liquid is mixed with so much solution of sodic sulphate as is necessary for the precipitation of the calcium as sulphate. The clear solution of sodic acetate is then evaporated, and the dry salt heated for a long time to 250°. Other products of dry distillation still admixed are thus either volatilised or carbonised. The salt, after cooling, is then dissolved in water, and the clear solution distilled with slight excess of sulphuric acid.

By both of these methods aqueous acetic acid is obtained, which can only be concentrated to a certain degree by fractional distillation.

572. In order to prepare acetic acid free from water, dried acetates have to be employed.

Alkaline acetates, freed from their water of crystallisation by fusion, are mixed with exactly sufficient sulphuric acid, or better with fused hydric sodic sulphate, and distilled:

$$2CH_3.CO.ONa + H_2SO_4 = 2CH_3.CO.OH + Na_2SO_4$$
$$CH_3.CO.ONa + NaHSO_4 = CH_3.CO.OH + Na_2SO_4.$$

The anhydrous lead salt also yields anhydrous acetic acid when treated by the last method.

573. Anhydrous acetic acid, *glacial acetic acid*, is in the cold a white mass of leafy crystals, which at +17° melts to a colourless, mobile liquid, having a strong acid smell and taste, and which blisters the skin. Its sp. gr. is 1·063 at 18°, its boiling point 118°, and its vapour density 2·09.

On adding some water to acetic acid, heat is evolved, and the specific gravity is increased, until by addition of one molecule of H_2O it reaches the maximum 1·079. There is thus formed acetyl trihydrate:

$$CH_3.CO.OH + H_2O = CH_3.C(OH)_3,$$

as a liquid which does not crystallise, and on heating to 123° boils with partial dissociation into its components. If this be diluted with water the density diminishes, so that an acid which contains about 50 % H_2O and 50 % $C_2H_3O_2$ (or 65 % $CH_3.C(OH)_3$ and 35 % H_2O) has the same density as the anhydrous acid.

Pure acetic acid, and also its aqueous solution, are very stable towards oxidising agents, being only attacked with difficulty by even potassic permanganate. Its vapour, when heated in air, burns with a slightly luminous flame. When passed through red-hot tubes, the vapour decomposes into numerous products, amongst which acetone and marsh gas occur largely:

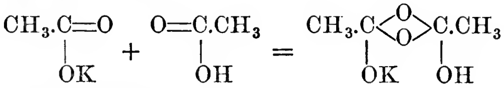
$$CH_3.CO.OH = CO_2 + CH_4$$
$$2CH_3.CO.OH = CO_2 + OH_2 + CH_3.CO.CH_3.$$

574. *Acetates.*—The neutral metallic salts of acetic acid, which are readily obtained by saturation of acetic acid with the basic hydrates, oxides, or carbonates, are without exception soluble in water, though not very readily in some cases; the alkaline salts are the most soluble. These melt on heating and decompose at above 300° into acetone and an alkaline carbonate:

$$2CH_3.CO.OK = CO(OK)_2 + CH_3.CO.CH_3.$$

The salts of polyvalent heavy metals decompose at lower temperatures, and, especially if not quite free from water of crystallisation, give off glacial acetic acid, and leave a difficultly soluble or insoluble basic salt, which decomposes at higher temperatures into metallic oxide, carbonic anhydride, and acetone.

575. *Potassic acetate*, $C_2H_3KO_2 = CH_3.CO.OK$, is a white deliquescent salt, which is readily soluble in absolute alcohol, and on heating fuses to a thick liquid, which solidifies on cooling to a leafy crystalline mass. On dissolving in concentrated acetic acid, and evaporating the excess, there crystallises out a salt, $C_2H_3O_2K,C_2H_4O_2$, in nacreous leaves or needles, which melt at 148° and at 200° split up into glacial acetic acid, which distils, and normal potassic acetate. This *potassic diacetate* is probably constituted as in the following formula, similarly to the polymeric aldehydes (§ 385):



$$\begin{array}{l}CH_3.C{=}O\\ \quad\ |\\ \quad OK\end{array} + \begin{array}{l}O{=}C.CH_3\\ \quad\ \ |\\ \quad\ OH\end{array} = \begin{array}{l}CH_3.C{<}^{O}_{O}{>}C.CH_3\\ \quad\ | \qquad\quad |\\ \quad OK \qquad OH\end{array}$$

Sodic acetate, $C_2H_3NaO_2$, crystallises from aqueous solutions in large rhombic prisms, $C_2H_3NaO_2,3H_2O$, which dissolve in 2·8 parts of cold and more readily in hot water. They suffer aqueous fusion at 100°, and lose their water of crystallisation at somewhat higher temperature. The dry salt fuses and behaves quite similarly to the potassic salt.

Ammonic acetate, $C_2H_3(NH_4)O_2$, is prepared directly from glacial acetic acid and ammonia. It resembles the potassic salt, but decomposes on heating into water and acetamide. Its solution loses ammonia on heating and becomes acid.

The salts of barium, strontium, calcium, magnesium, zinc, &c., are soluble, and in part crystallise well.

576. *Lead Salts.*—*Normal plumbic acetate, plumbic diacetate*, $(CH_3.CO.O)_2Pb,3H_2O$, known in commerce as *sugar of lead*, is obtained by dissolving litharge (PbO) in distilled vinegar, and crystallises in tetragonal prisms of first sweet, but later nauseous metallic taste. It dissolves in 1½ part of water and eight parts of alcohol. The crystals effloresce in dry air. They fuse in their water of crystallisation at 75° and lose the same quickly at 100°. The then solid mass fuses again at higher temperatures, loses ⅓ of its acid in the form of carbonic anhydride and acetone, and solidifies suddenly to a greyish white mass of basic salt, which decomposes at higher temperatures into plumbic oxide, carbonic anhydride, and acetone.

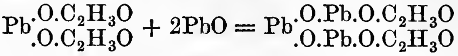
Basic salts are also prepared by digesting plumbic diacetate with plumbic oxide.

Plumbic monacetate :

$$2HO.Pb.O.C_2H_3O,H_2O, \text{ or } C_2H_3O.O.Pb.O.Pb.O.C_2H_3O,2H_2O,$$

is formed by boiling a solution of 1 part of sugar of lead with 6 parts of plumbic oxide, and separates in crystals on addition of alcohol to the filtered solution.

If a solution of plumbic diacetate be boiled with excess of plumbic oxide, *triplumbic acetate* is formed :



$$Pb\begin{matrix}.O.C_2H_3O\\.O.C_2H_3O\end{matrix} + 2PbO = Pb\begin{matrix}.O.Pb.O.C_2H_3O\\.O.Pb.O.C_2H_3O\end{matrix}$$

as a salt readily soluble in water, of strongly alkaline reaction, which on addition of alcohol is precipitated in fine transparent needles.

Still more basic salts are obtained as white precipitates when plumbic acetate is decomposed by a large excess of ammonia, e.g. *hexplumbic acetate :*

$$HO.Pb.O.Pb.O.Pb.O.C_2H_3O,H_2O.$$

All the basic acetates are decomposed by carbonic anhydride into basic carbonate (white lead) and normal salt, and this latter also in dilute aqueous solution is partly decomposed by carbonic anhydride into carbonate and free acetic acid.

577. *Copper Salts.*—In addition to the normal salt numerous basic salts are known.

Cupric diacetate, termed distilled verdigris, obtained by dissolving cupric oxide in acetic acid, crystallises below $+8°$ in large blue prisms of the formula $Cu(O.CO.CH_3)_2,5H_2O$, above this temperature in dark green rhombic prisms, $Cu(O.C_2H_3O)_2,H_2O$. It is moderately soluble in water ; the dilute aqueous solution partly decomposes even in the cold, but more readily on boiling, into free acetic acid and difficultly soluble basic salt. Ordinary *verdigris* is a mixture of different basic salts. It is prepared on the large scale by exposing plates of copper to the air for some time in contact with acetic acid or the marc of grapes.

On heating a mixture of equal molecules of cupric diacetate and lime with water, and then adding acetic acid until all is dissolved, there separates on evaporation a double salt of the formula $Ca(O.C_2H_3O)_2,Cu(O.C_2H_3O)_2,8H_2O$ in deep blue octagonal prisms of the quadratic system.

By mixing boiling solutions of cupric diacetate and arsenious acid a precipitate is formed which, after remaining some time under the liquid, changes into a beautiful green powder of *Schweinfurth green.* This is a *cupric arseno-acetate* of the formula $Cu_2(O.AsO)_3(C_2H_3O_2)$.

578. *Argentic acetate,* $Ag.O.C_2H_3O$, is obtained on mixing argentic nitrate with a strong solution of an alkaline acetate, as a spongy crystalline precipitate, which dissolves to a greater extent in hot water and separates again on cooling in colourless nacreous plates and flexible needles.

579. *Iron Salts.—Ferrous diacetate,* $Fe(C_2H_3O_2)_2$, prepared by dissolving iron in acetic acid, crystallises in green prisms, which dissolve readily and are quickly oxidised in air. Several ferric salts are known. By dissolving freshly precipitated ferric hydrate in acetic acid, a deep brown red solution of *normal ferric acetate :*

$$Fe_2(O.C_2H_3O)_6,$$

is obtained, which—evaporated at a low temperature—yields a black-brown syrup, also soluble in alcohol. On boiling the dilute aqueous solution all the iron is precipitated in the form of an amorphous basic salt, whilst acetic acid is set free.

580. *Aluminium Salts.—Normal aluminic acetate,* $Al_2(O.C_2H_3O)_6$, is obtained in aqueous solution by double decomposition of aluminic sulphate and plumbic acetate. It behaves similarly to the solution of the corresponding ferric salt, e.g. on boiling precipitates all its aluminium as a strongly basic amorphous salt.

Propionic Acid, $C_3H_6O_2$.

581. *Propionyl hydrate,* $HO.C_3H_5O$, or *ethyl carbonic acid,* $HO.CO.C_2H_5 = HO.CO.CH_2.CH_3$. Propionic acid was first obtained by oxidation of metacetone with chromic and sulphuric acids, and was therefore termed *metacetonic acid.* It is formed in small quantity in the dry distillation of wood, in the decomposition of sugar with concentrated potassic hydrate, the action of carbonic oxide upon sodic ethylate:

$$CO + NaOC_2H_5 = NaO.CO.C_2H_5,$$

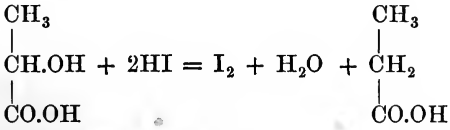
&c. A better yield is obtained from carbonic anhydride and sodium ethyl:

$$CO_2 + Na.C_2H_5 = NaO.CO.C_2H_5,$$

but it is most conveniently prepared by decomposition of aceto-nitrile by alkalies or strong acids in concentrated aqueous solutions:

$$C_2H_5.CN + H_2SO_4 + 2H_2O = NH_4.HSO_4 + C_2H_5.CO.OH.$$

It is further obtained by reduction of fermentation lactic acid by heating with concentrated hydriodic acid:



$$\begin{array}{l} CH_3 \\ | \\ CH.OH \\ | \\ CO.OH \end{array} + 2HI = I_2 + H_2O + \begin{array}{l} CH_3 \\ | \\ CH_2 \\ | \\ CO.OH \end{array}$$

also from aceto-methacetic acid (§ 559, 4).

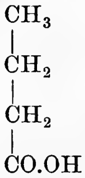
Other methods of formation, as from β-iodo-propionic acid, &c., will be mentioned later.

Propionic acid is a liquid resembling acetic acid, of sp. gr. ·991 at 25° and boiling at 140·5°. It mixes in every proportion with water, but is separated as an oily layer on saturating the solution with calcic chloride.

The *normal propionates* are all soluble in water, in part even more readily than the corresponding acetates. The baric salt, $Ba(O.C_3H_5O)_2,H_2O$, crystallises in rhombic prisms. Normal plumbic propionate does not crystallise, or only with the greatest difficulty; the silver salt, $AgO.CO.C_2H_5$, crystallises from saturated solutions in tufts of colourless needles, which require 120 times their weight of water at 18° for solution and blacken at 100°.

Butyric Acids, $C_4H_8O_2$.

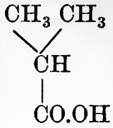
582. Both possible isomers:



$$\begin{matrix} CH_3 \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CO.OH \end{matrix}$$

Normal butyric acid, or propyl carbonic acid.

and



Isobutyric acid, or isopropyl carbonic acid.

are known.

1. *Normal butyric acid*, or *fermentation butyric acid*:

$$CH_3.CH_2.CH_2.CO.OH,$$

occurs as fat (glyceric salt) in butter, as hexylic salt in the oil of *Heracleum giganteum* (§ 171), as octylic salt in the seeds of *Pastinaca sativa*. It occurs also in the free state or in the form of salts in many animal liquids, e.g. in sweat and muscle juice, and as a product of the putrefaction and oxidation of many albuminoids and of gelatine. It is prepared by the oxidation of normal primary butylic alcohol, by boiling normal propylic cyanide with potassic hydrate, and by the decomposition of ethylic aceto-ethyl acetate.

It is obtained readily and in large quantity by a peculiar fermentation of sugar. A solution, prepared at the boiling temperature, and afterwards cooled, of three kilograms of cane sugar and fifteen grams tartaric acid in fifteen kilograms of water is, after standing for several days, mixed with 120 grams of putrefying cheese in four kilograms of sour milk; one and a half kilogram of powdered chalk is added, and the mixture then allowed to stand and kept at a temperature of 30°–35°. After about a week or a week and a half the mixture forms a crystalline paste of calcic lactate, which slowly becomes again liquid, carbonic anhydride and hydrogen being evolved and calcic butyrate formed:

$$2\underset{\text{Calcic lactate.}}{(C_3H_5O_3)_2Ca} + H_2O = \underset{\text{Calcic butyrate.}}{(C_4H_7O_2)_2Ca} + CaCO_3 + 3CO_2 + H_2.$$

On addition of sodic carbonate all the calcium is precipitated as carbonate, whilst sodic butyrate remains in solution. This is filtered, evaporated considerably, and carefully decomposed by a slight excess of sulphuric acid, whereby the crude butyric acid collects as an oily layer on the surface. This is removed, dried by means of calcic chloride, and purified by fractional distillation. As in the fermentation, together with much acetic acid, some caproic acid and also higher homologues are formed, the butyric acid, if required chemically pure, must be submitted to further treatment. That portion of the crude acid distilling between 155° and 165° is converted into the calcic salt by saturation with thin milk of lime, and the filtered solution evaporated by boiling. Calcic butyrate then separates on the surface as a leafy crystalline scum; this is skimmed off, collected on a filter, washed with boiling water, and then pressed. The pure calcic butyrate so obtained is then converted into the sodic salt, this decomposed by concentrated sulphuric acid, and the oily acid which separates rectified.

Pure butyric acid is a colourless liquid of unpleasant, penetrating, rancid odour, and solidifies in the cold to a crystalline mass of nacreous lustre. It melts at about 0° and boils at 163°; its sp. gr. is ·958 at 14°. It mixes in every proportion with water, but is separated from this solution by saturation with readily soluble salts, such as calcic chloride, as an oil containing water, probably *butyric trihydrate*, $C_3H_7.C(OH)_3$. It is only attacked with difficulty by oxidising agents, chromic and sulphuric acids first oxidising it at about 200° to acetic and carbonic acids:

$$CH_3.CH_2.CH_2.CO.OH + 2K_2Cr_2O_7 + 8H_2SO_4 = CH_3CO.OH + 2CO_2 + 10H_2O + 2K_2Cr_2(SO_4)_4.$$

By more gentle oxidation propylic butyrate, propionic acid, &c., are formed (§ 565).

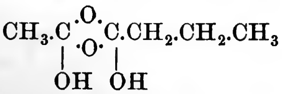
Butyrates.—The butyrates are soluble in water and alcohol, are crystallisable, and smell of butyric acid when moist. Even those readily soluble are only slowly moistened when thrown on cold water, and exhibit a rotary movement during solution.

Calcic butyrate, $Ca(O.CO.CH_2.CH_2.CH_3)_2,H_2O$, is dissolved by three and a half times its weight of water at 14°, but very difficultly at 70°, so that a cold saturated solution, when heated to this temperature, separates nearly all its salt in brilliant leafy crystals, which disappear again on cooling.

Baric butyrate, $Ba(O.C_4H_7O)_2$, crystallises in readily soluble nacreous plates.

Argentic butyrate, $AgO.C_4H_7O$, is precipitated on mixing not too dilute solutions of other butyrates with argentic nitrate, in colourless scales, which require more than 400 parts of water at 14° for solution.

On mixing solutions of butyrate and acetate of the same metal and evaporating, crystalline compounds are frequently obtained, containing both bodies in equal molecules. These butyrato-acetates (which are polymeric with the propionates) appear to have a similar constitution to the diacetates (§ 575):



$$\begin{array}{l} CH_3.\underset{\displaystyle OH}{\underset{|}{C}}\overset{.O.}{\underset{.O.}{}}\underset{\displaystyle OH}{\underset{|}{C}}.CH_2.CH_2.CH_3 \end{array}$$

2. *Isobutyric acid*, $\genfrac{}{}{0pt}{}{CH_3}{CH_3}{>}CH.CO.OH$, occurs in St. John's bread (the fruit of *Ceratonia siliqua*), and is formed from isobutylic alcohol or isobutyric aldehyde on oxidation, also from isopropylic cyanide by boiling with acids or alkalies. It is separated as an oil by addition of concentrated sulphuric acid to its salts. Its sp. gr. is ·9503 at 20°.

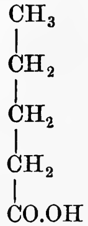
It boils at 154° and requires five times its weight of water at 20° for solution. It is readily oxidised by chromic and sulphuric acids to acetic acid and carbonic anhydride.

Calcic isobutyrate, $Ca[O.CO.CH:(CH_3)_2]_2,5H_2O$, crystallises in long prisms, which dissolve much more readily in hot than in cold water.

Argentic isobutyrate, $AgO.CO.CH:(CH_3)_2$, crystallises in plates, which require 110 parts of water at 16° for solution.

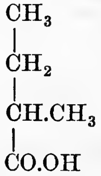
Valeric Acids, $C_5H_{10}O_2$.

583. All four possible isomeric valeric acids :



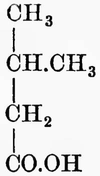
$$\begin{array}{l} CH_3 \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CO.OH \end{array}$$

Normal valeric acid,
butyl carbonic acid,
or propyl acetic acid.



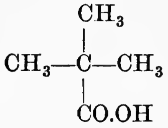
$$\begin{array}{l} CH_3 \\ | \\ CH_2 \\ | \\ CH.CH_3 \\ | \\ CO.OH \end{array}$$

β-butyl carbonic acid,
meth-eth-acetic acid,
or α-methyl butyric acid.



$$\begin{array}{l} CH_3 \\ | \\ CH.CH_3 \\ | \\ CH_2 \\ | \\ CO.OH \end{array}$$

Isovaleric acid,
isobutyl carbonic acid,
β-methyl butyric acid,
isopropyl acetic acid.



$$\begin{array}{c} CH_3 \\ | \\ CH_3—C—CH_3 \\ | \\ CO.OH \end{array}$$

Trimeth-acetic acid,
or trimethyl carbin-carbonic acid.

have been prepared.

1. *Normal valeric acid* is formed by the oxidation of normal primary amylic alcohol and by boiling normal butylic cyanide with alkalies. It is liquid, smells like butyric acid, has sp. gr. ·9577 at 0°, and does not solidify at −16°. It boils at 184°–185°, and dissolves in twenty-eight times its weight of water at 16°.

Baric valerate, $Ba(O.CO.CH_2.CH_2.CH_2.CH_3)_2$, crystallises in plates, which dissolve in six times their weight of water at 10°.

Calcic valerate, $Ca(O.CO.C_4H_9)_2,H_2O$, crystallises in fatty leafy crystals, dissolves in twelve parts of water at 20°, and, like calcic butyrate, separates in great part on heating the solution to 70°.

2. *Isovaleric acid*, $\begin{array}{l}CH_3\\CH_3\end{array}\!\!>CH.CH_2.CO.OH$, occurs in the roots of *Valeriana* and *Angelica officinalis* (in the latter together with angelic acid) and in the berries and bark of *Viburnum Opulis*. It is obtained from these parts of the plants by fine division and distillation with water. It occurs as fat in the tears of *Delphinus globiceps*. It is formed by the oxidation of fats of higher homologous acids and by

the putrefaction of albuminoids; e.g. it occurs largely in rotten cheese. It is obtained synthetically by boiling isobutylic cyanide with alkalies and by oxidation of isoamylic alcohol.

This succeeds best when five parts of potassic dichromate are placed with four parts of water in a retort turned upwards and provided with an inverted condenser, and a mixture of one part of fermentation amylic alcohol and four parts of sulphuric acid then added. The reaction soon starts of itself with lively ebullition. Later it is heated to boiling until no oily streaks of isoamylic aldehyde can be observed in the neck of the retort or the condenser. The retort is then turned downwards, and the valeric acid, together with water, distilled over. The distillate is saturated with sodic hydrate, the oily isoamylic isovalerate which separates removed, the salt solution evaporated to dryness and treated with four-fifths of its weight of sulphuric acid that has previously been diluted with half the quantity of water. The oily valeric acid is then separated, dried with calcic chloride, and purified by distillation.

Isovaleric acid is a thin, colourless oil of unpleasant valerian-like odour. It has sp. gr. ·947 at 0°; it boils at 175°. The anhydrous acid, on shaking with water, takes up a molecule of the latter:

$$(CH_3)_2CH.CH_2.CO.OH + OH_2 = (CH_3)_2CH.CH_2.C(OH)_3,$$

yielding isovaleryl trihydrate, which is not completely decomposed on distillation and dissolves in thirty parts of water.

The metallic isovalerates have a fatty feeling, smell of valeric acid when damp, are mostly readily soluble in water, and in part crystallise therefrom with difficulty.

Baric isovalerate, $Ba[O.CO.CH_2.CH(CH_3)_2]_2,H_2O$, forms thin prisms or plates, which dissolve in two parts of cold water, but in their own weight of water at 22°.

Zincic isovalerate, $Zn(O.C_5H_9O)_2$, forms nacreous scales, which are more soluble in alcohol than in water. The salt is officinal.

Argentic isovalerate, $AgO.C_5H_9O$, crystallises in brilliant leafy plates, which require 450 parts of water for solution.

3. *Eth-meth-acetic acid*, $CH(CH_3)(C_2H_5).CO.OH$, has been prepared synthetically by distilling ethylic eth-meth-aceto-acetate with sodic ethylate and saponification of the ethylic eth-meth-acetate so formed. The same acid appears to be formed by oxidation of optically active fermentation amylic alcohol (§ 170) with potassic dichromate and sulphuric acid. Obtained by this latter method, it rotates the plane of polarisation strongly to the right, whilst that prepared synthetically appears to be optically inactive. Otherwise the acids from both sources agree in properties. Eth-meth-acetic acid is a thin liquid of boiling point 173°. The argentic salt crystallises from hot water in feathery needles; the baric salt refuses to crystallise, leaving a gum-like mass on evaporation.

4. *Trimeth-acetic acid*, *pseudo-valeric acid*, or *pinalic acid*, $(CH_3)_3{:}C.CO.OH$, is obtained by heating trimethyl-carbin-cyanide with alkalies, or better with concentrated hydrochloric acid, to 100°, and by oxidation of pinacoline (§ 504, 3) with chromic and dilute sulphuric acids. The crude acid is converted into the potassic salt, this evaporated to dryness, and decomposed with sulphuric acid.

Trimeth-acetic acid then separates as an oil, which crystallises on cooling.

Trimeth-acetic acid forms leafy crystals, melting at 34°–35, and boils at 161°. It requires forty times its weight of water for solution. Its baric salt, $Ba[O.CO.C:(CH_3)_3]_2,5H_2O$, and calcic salt:

$$Ca(O.C_5H_9O)_2,4H_2O,$$

crystallise in silky needles, which are readily soluble.

Caproic Acids, or Amyl Carbonic Acids, $C_6H_{12}O_2$.

584. Of the eight possible isomeric amyl carbonic acids only the following have yet been prepared:—

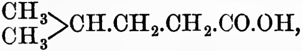
1. *Normal caproic acid,* $CH_3.CH_2.CH_2.CH_2.CH_2.CO.OH$, occurs in nature partly in the free state (in sweat and in the blood of *Satyrium hircinum*), partly in several fats as glyceric salts (in butter and cocoa-nut oil), and is formed from albuminoids and acids richer in carbon by oxidation. It is obtained from normal primary hexylic alcohol by chromic and sulphuric acids, and from normal primary amylic iodide by conversion into the cyanide and decomposition of this latter by alkalies. It is formed also in pretty considerable quantity in the butyric fermentation of sugar. In order to purify it the calcic or baric salt is prepared, recrystallised, and the caproic acid separated by addition of the hydrochloric acid.

Caproic acid is an oily liquid of faint, unpleasant odour, not miscible with water, having at 0° sp. gr. ·945. On strong cooling it solidifies to a crystalline mass, which melts at $-2°$. It boils at 205°.

Calcic caproate, $Ca(O.CO.CH_2.CH_2.CH_2.CH_2.CH_3)_2,H_2O$, crystallises in plates, which dissolve in 36–37 parts of water at 19°.

Baric caproate, $Ba(O.C_6H_{11}O)_2$, requires about twelve times its weight of water at 20° for solution.

Argentic caproate is nearly insoluble in water.

2. *Isocaproic acid,*  $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH.CH_2.CH_2.CO.OH$, or *isoamyl carbonic acid,* is obtained from isoamylic cyanide by decomposition with alcoholic potassic hydrate and by saponification of ethylic aceto-isobutyl acetate. It is an oil resembling the normal acid, of sp. gr. ·931, and boiling at 199°–200°.

Calcic isocaproate, $Ca[O.CO.CH_2.CH_2.CH:(CH_3)_2]_2,3H_2O$, crystallises in plates, and requires nine parts of water at 18·5° for solution.

3. If the secondary isoamylic iodide be heated in alcoholic solution with potassic cyanide, the resulting cyanide decomposed by alkali, and the alkaline salt treated with acid, *methyl-isopropyl acetic acid,*  $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH.CH\!\!<\begin{matrix}CH_3\\CO.OH\end{matrix}$, is obtained in the free state as an oil of fearful odour, which has been little investigated. Its calcic salt is difficultly soluble in hot water and crystallises in scales.

4. *Dieth-acetic acid,*  $\begin{matrix}CH_3.CH_2\\CH_3.CH_2\end{matrix}\!\!>CH.CO.OH$, is obtained by saponification of its ethylic salt, which latter is a product of the splitting up of aceto-diethyl acetate. The free acid is an oil; the baric salt, $Ba[O.CO.CH(C_2H_5)_2]_2$, is crystalline and readily soluble in

water. The argentic salt, $AgO.CO.CH(C_2H_5)_2$, is also soluble, and crystallises in asbestos-like, silky needles.

5. *Dimeth-eth-acetic acid*, $C(CH_3)_2(C_2H_5).CO.OH$, is obtained by heating dimethyl-ethyl carbin-cyanide with strong hydrochloric acid at 100°. It is a colourless liquid, insoluble in water, boiling at 187°.

Baric dimeth-eth-acetate, $(C_5H_{11}CO.O)_2Ba,5H_2O$, crystallises in large transparent plates. The zincic salt forms transparent prisms, and the silver salt fine silky needles.

Heptylic Acids, or Hexyl Carbonic Acids, $C_7H_{14}O_2$.

585. Only two of the numerous possible hexyl carbonic acids have been accurately investigated.

Normal heptylic acid, or *œnanthylic acid :*

$$CH_3.CH_2.CH_2.CH_2.CH_2.CH_2.CO.OH,$$

is obtained from normal primary hexylic iodide by conversion into normal primary hexylic cyanide by treatment with potassic cyanide and decomposition with alcoholic potassic hydrate, and also by the oxidation of normal primary heptylic alcohol. It is prepared most readily by the oxidation of its aldehyde, œnanthol (§ 400). It forms a colourless oil of faint odour and of sp. gr. ·9345 at 0°, solidifying in the cold to a crystalline mass, melting at $-10{\cdot}5°$ and boiling at 223°–224°.

The *calcic salt*, $Ca(O.C_7H_{13}O)_2,H_2O$, crystallises in tufts of needles, which dissolve in 106 parts of water at 8°.

Isœnanthylic acid, probably $(CH_3)_2 : CH.CH_2.CH_2.CH_2.CO.OH$, is prepared by oxidation of isœnanthylic alcohol. It is a colourless, oily liquid of peculiar and disagreeable odour; it boils at 210°–213°.

Another isœnanthylic acid, boiling at 220°, is obtained by heating a mixture of sodic ethylate and isovalerate in carbonic oxide.

Acids Richer in Carbon.

586. In most cases only one representative of each higher member of the series is known, although the number of possible isomers increases enormously with each additional carbon atom. With few exceptions they are prepared from the fats, and those so obtained appear to be normal acids, $CH_3(CH_2)_nCO.OH$, as on oxidation with chromic and sulphuric acids they yield normal acids poorer in carbon. They are insoluble in water, soluble in alcohol and ether, and are crystallisable. Their alkali salts are true soaps, i.e. dissolve in little water to a clear solution, but are partially decomposed by much water, with clouding and liberation of some alkali, to liquids which froth strongly on shaking. The other metallic salts are most difficultly soluble or insoluble in water, but mostly soluble in alcohol.

587. *Octylic* or *caprylic acid*, $C_8H_{16}O_2 = C_7H_{15}.CO.OH$, the carbonic acid of normal primary heptyl, is prepared by oxidation of normal primary octylic alcohol (§ 173), and occurs in wine fusel oils, as a fat in butter, in cocoa-nut oil, and in other vegetable fats.

Caprylic acid crystallises in fine needles or plates, which melt between 16° and 17° and smell like sweat. It boils at 232°–234°.

Its baric salt requires fifty parts of cold, and more than 100 parts of hot, water for solution.

An *iso-octylic acid,* $C(CH_3)_3.CH_2.CH(CH_3).CO.OH$, is prepared by oxidation of diisobutylene; it is an oily liquid, boiling, apparently with some decomposition, at 205°–218°.

588. *Nonylic acid,* or *pelargonic acid,* $C_9H_{18}O_2 = C_8H_{17}.CO.OH$, occurs in the essential oil of *Pelargonium roseum,* and is obtained by oxidation of methyl-nonyl ketone, the essential oil of *Ruta graveolens* (§ 455), with nitric acid, and also by acting on ethylic heptyl aceto-acetate with solid potassic hydrate and acidulation of the resulting salt. It is solid below 12° and boils at 253°–254°.

Methyl-hexyl acetic acid, $C_6H_{15}.CH(CH_3).CO.OH$, is prepared from the cyanide derived from methyl-hexyl carbinol. It is a colourless oil, boiling at 245°.

589. *Capric acid,* $C_{10}H_{20}O_2 = C_9H_{19}.CO.OH$, occurs as glyceric salt in butter, in cocoa-nut oil, and all fats which contain caproic or caprylic acids. It is solid and crystalline, melts at 30°, boils at 270°, and has a faint, goat-like odour. The baric salt is scarcely soluble even in hot water.

590. *Undecylic acid,* $C_{11}H_{22}O_2 = C_{10}H_{21}.CO.OH$, obtained by the oxidation of methyl-undecyl ketone (§ 455*a*), melts at 28·5° and boils at 212°–213° under a pressure of 100 mm.

591. *Lauric acid,* $C_{12}H_{24}O_2 = C_{13}H_{23}CO.OH$, obtained from the fat of pichurium beans, the fruit of *Laurus nobilis,* butter, cocoa-nut oil, &c., crystallises in spear-like, silky needles, which melt at 43·6° and have sp. gr. ·883. It boils at 225·5° under a pressure of 100 mm., but is partially decomposed on distillation at ordinary pressures.

592. *Tridecylic acid,* $C_{13}H_{26}O_2 = C_{12}H_{25}.CO.OH$, obtained by oxidation of methyl-tridecyl ketone (§ 455*b*), melts at 45° and solidifies a little below this to scaly crystals. It boils at 236° under a pressure of 100 mm.

593. *Myristic acid,* $C_{14}H_{28}O_2 = C_{13}H_{27}.CO.OH$, forms a glyceric salt, the chief constituent of muscat butter (the fat of the fruit of *Myristica moschata*), but is also prepared from spermaceti, cocoa-nut oil, and other fats. It crystallises from alcohol in silky needles, which melt at 54°. Under a pressure of 100 mm. it boils at 248°.

594. *Pentadecylic acid,* $C_{15}H_{30}O_2 = C_{14}H_{29}.CO.OH$, prepared by the oxidation of methyl-pentadecyl ketone (§ 455*c*), forms nacreous scales, which melt at 51° and boil at 257° under a pressure of 100 mm.

595. *Palmitic acid,* $C_{16}H_{32}O_2 = C_{15}H_{31}.CO.OH$, occurs as a glyceric salt in nearly all animal and vegetable fats. In the solid animal fats it occurs mostly with stearic and oleic acids, in olive oil with little but the latter. It is obtained from its mixture with stearic acid (stearine candles' material) by the method of fractional precipitation (§ 563), and more readily from olive oil. This is saponified by boiling with sodic hydrate, when the thick solution contains glycerine and the soda soaps of oleic and palmitic acids. These are precipitated on saturating the water with common salt, separated from the salt solution, dissolved in pure water, and precipitated by addition of plumbic acetate as plumbic oleate and palmitate (lead plaster). From this mixture the plumbic oleate is completely removed by extraction with ether, and the residual plumbic palmitate decomposed by alcoholic hydrochloric acid. The alcoholic liquid, filtered from plumbic chloride, yields, when precipitated with water, nearly pure palmitic acid, which must be recrystallised several times from alcohol.

Palmitic acid is also obtained by heating cetylic alcohol with solid alkalies:

$$C_{15}H_{31}.CH_2.OH + HOK = 2H_2 + C_{15}H_{31}.CO.OK,$$

and from oleic acid by heating with potassic hydrate.

Palmitic acid crystallises in needles, which melt at 62° and resolidify in leafy crystals on cooling; it boils at 268·5° under a pressure of 100 mm.

The alkaline salts are soluble in alcohol and little water, and are true soaps; all other metals yield insoluble soaps with palmitic acid.

An isomeric acid, *diheptyl acetic acid*, $CH(C_7H_{15})_2.CO.OH$, is prepared by action of ethylic diheptyl aceto-acetate on solid potassic hydrate. It forms a paraffin-like mass, melting at 26°–27° and boiling at 240°–250° under 80–90 mm. pressure.

596. *Margaric acid, cetyl carbonic acid :*

$$C_{17}H_{34}O_2 = C_{15}H_{31}.CH_2.CO.OH,$$

is obtained from cetylic cyanide by boiling with potassic hydrate solution, and also by oxidation of methyl-heptadecyl ketone (§ 455*c*). It resembles palmitic acid, melts at 59·9°, and boils at 277° under a pressure of 100 mm.

597. *Stearic acid*, $C_{18}H_{36}O_2$, or $C_{17}H_{35}.CO.OH$, occurs especially in the solid animal fats, and, mixed with palmitic acid, forms the material used for making *stearine candles.* To prepare this latter, solid animal fats are heated with water, to which a very small quantity of sulphuric acid has been added, for some time to 200°. According to the equation :

$$C_3H_5(O.C_nH_{2n-1}O)_3 + 3H_2O = C_3H_5(OH)_3 + 3HO.C_nH_{2n-1}O,$$

the fats are decomposed into glycerine, which remains dissolved in the excess of water, and a mixture of stearic, palmitic, and oleic acids, which float on the surface of the liquid. This is removed after solidification, and strongly compressed by hydraulic presses, first at ordinary temperature, later at 30°–40°, in order to remove the liquid oleic acid. The mixture of solid acids melts at a lower temperature than palmitic acid, and, after addition of some wax or paraffin to hinder crystallisation, is employed for stearine candles.

Pure stearic acid, which can be prepared from this mixture by the method of fractional precipitation, melts at 69·2°, solidifies in scaly crystals, and is obtained from alcoholic solutions in brilliant plates.

At ordinary pressure stearic acid only distils with decomposition : at a pressure of 100 mm. it distils unaltered at 287°, and also passes over at 250°–350° in a current of super-heated steam.

A fused and resolidified mixture of equal molecules of stearic and palmitic acid, which contains the elements in the same proportion as margaric acid :

$$C_{18}H_{36}O_2 + C_{16}H_{32}O_2 = C_{34}H_{68}O_4 = 2C_{17}H_{34}O_2,$$

was taken for margaric acid before the method of fractional precipitation was known. It melts at about 60° and solidifies to a needle-formed crystalline mass. A mixture of two parts palmitic acid and one part stearic acid fuses at 55°.

598. *Arachidic acid,* $C_{20}H_{40}O_2$, is found in the fat of earth nut (*Arachis hypogaea*), in butter, and some other fats. It crystallises in brilliant plates, which melt at 75°.

599. *Behenic acid,* $C_{22}H_{44}O_2$, prepared from oil of ben, the fat of the fruit of *Moringa-nux Behen,* melts at 76°.

600. *Hyaenic acid,* $C_{25}H_{50}O_2$, is separated from the fat of the glandular pouches of *Hyaena striata* as an acid melting at 77°.

601. *Cerotic acid,* $C_{27}H_{54}O_2$, forms the chief constituent of bees'-wax, and is extracted therefrom by boiling with ether, whilst mellissylic palmitate remains undissolved. On cooling the hot filtered liquid, crude cerotic acid separates, and is collected on a filter and pressed. It is then dissolved in hot alcohol, precipitated with plumbic acetate, and the crude plumbic cerotate so obtained purified by treatment with alcohol and ether. It is decomposed by hot acetic acid, and the separated cerotic acid recrystallised from alcohol.

It is also obtained by the saponification of Chinese wax (cerylic cerotate), and by oxidation of cerylic alcohol by fusing with potassic hydrate.

Cerotic acid crystallises from alcohol in small grains, which melt at 79°.

602. *Mellissic acid,* $C_{30}H_{60}O_2$, is prepared by oxidation of mellissylic alcohol with fused alkalies :

$$C_{29}H_{59}.CH_2.OH + HOK = 2H_2 + C_{29}H_{59}.CO.OK.$$

It is an indistinctly crystalline, wax-like substance, melting at 91°.

Halogen Compounds of the Acidoxyls.

603. The organic salts are not altered by the halogen hydro-acids even in the absence of water; in the latter case, however, if phosphoric anhydride be also present, reaction occurs. A mixture of glacial acetic acid and phosphoric anhydride yields acetyl chloride when heated with dry hydrochloric acid gas :

$$CH_3.CO.OH + P_2O_5 + HCl = 2HPO_3 + CH_3.CO.Cl.$$

The acid chlorides are obtained more readily by the action of the halogen compounds of phosphorus on the acids or their anhydrides.

Phosphoric chloride or bromide react with one molecule of the acid, yielding phosphoric oxy-haloid, acid oxy-haloid, and halogen hydro-acid, the reaction starting at the ordinary temperature and evolving much heat :

$$C_nH_{2n+1}.CO.OH + PCl_5 = POCl_3 + C_nH_{2n+1}.CO.Cl + HCl.$$

For this purpose phosphoric chloride is placed in a retort, whose neck is turned up and attached to an inverted condenser; the acid is then allowed to flow in slowly through a funnel tube provided with a stop-cock, and passed through the tubulus of the retort. After completion of the reaction the liquid products are separated by fractional distillation.

On bringing together one molecule of a phosphoric oxy-trihaloid and two molecules of a dried alkali salt of an organic acid, an energetic reaction ensues, in which acidoxyl haloid, metallic haloid, and metaphosphate are formed:

$$POCl_3 + 2NaO.CO.C_{n'}H_{2n'+1} = NaO.PO_2 + NaCl$$
$$+ 2Cl.CO.C_{n'}H_{2n'+1}.$$

The reactions between phosphorus trihaloids and acids, which can also be employed, require to be assisted by heat, but, from the non-formation of any volatile phosphorus compound, yield the pure acidoxyl haloid on careful distillation.

Acidoxyl iodides cannot be prepared from the acids themselves, as these, on treatment with phosphorus iodide, yield iodine, and are further decomposed; but by treatment of the acid anhydrides with phosphorus triiodide, the acidoxyl iodides are formed, e.g.

$$3(CH_3.CO)_2O + 2PI_3 = P_2O_3 + 6CH_3.CO.I,$$

the phosphorus trioxide then acting further on a portion of the anhydride.

Instead of employing the haloid compounds of phosphorus, the dried acids or anhydrides may be mixed with amorphous phosphorus and then treated with the halogen.

604. The acidoxyl haloids are mostly heavy liquids which fume in the air. When added to water, they generally sink in oily globules, but soon decompose with it into halogen hydro-acid and fatty acid, the reaction being generally violent:

$$C_nH_{2n+1}.CO.Cl + H_2O = C_nH_{2n+1}.CO.OH + HCl.$$
$$CH_3.CO.I + H_2O = CH_3.CO.OH + HI.$$

The halogen is much less firmly united to carbon in these compounds than in the alkyl haloids, which do not contain oxygen united to the same carbon atom. In this respect the halogen compounds of oxygenated organic radicals behave like those of the inorganic acid radicals.

The reaction of the acid haloids upon alcohols is similar to that with water, as the alcoholic salt of the acid and halogen hydro-acid are formed with much evolution of heat; or, if excess of alcohol be present, the latter forms with it alkyl haloid and water. The first reaction occurs according to the equation:

$$C_nH_{2n+1}.OH + Cl.CO.C_{n'}H_{2n'+1} = HCl + C_nH_{2n+1}.O.CO.C_{n'}H_{2n'+1}.$$

605. *Formyl haloids* are not known. If, for instance, phosphoric pentachloride reacts on pure formic acid, carbonic oxide is evolved:

$$H.CO.OH + PCl_5 = POCl_3 + HCl + HCO.Cl = POCl_3$$
$$+ 2HCl + CO.$$

606. *Acetyl Haloids.—Acetic chloride*, or *chlor-acetyl*, $CH_3.CO.Cl$, is a colourless liquid of penetrating odour, fuming in the air, has sp. gr. 1·125, and boils at 55°. It first sinks in water, but soon decomposes with violence into acetic and hydrochloric acids. *Acetic bromide*, or *brom-acetyl*, $CH_3.CO.Br$, resembles the chloride, but boils at 81°. *Acetic iodide*, or *iodo-acetyl*, $CH_3.CO.I$, is a liquid boiling at

108°; it is always coloured brown by free iodine, and decomposes on exposure to light with separation of iodine and further changes of the organic residue.

607. *Propionic chloride,* or *chlor-propionyl,* $CH_3.CH_2.CO.Cl$, boils at 80°, *propionic bromide* at 96°–98°, and *propionic iodide,* $CH_3.CH_2.CO.I$, at 127°–128°. All three fume on exposure to air.

Butyric chloride, or *chlor-butyryl,* $CH_3.CH_2.CH_2.CO.Cl$, boils at 101°; *isobutyric chloride,* $(CH_3)_2CH.CO.Cl$, at 92°.

Isovaleric chloride, or *chlor-isovaleryl,* boils at 115°, and has sp. gr. 1·005 at 6°.

Ethereal Salts.

608. *Methods of Preparation.*—On mixing a fatty acid with alcohol, only a feeble and incomplete reaction occurs; on heating the mixture to higher temperatures it occurs to a greater degree, so that considerable quantities of the salt, together with water, are formed, but even then considerable quantities of the ingredients remain unaltered. The process is represented by the following equation:

$$aC_nH_{2n+1}.OH + aHO.CO.C_{n'}H_{2n'+1} = bH_2O$$
$$+ bC_nH_{2n+1}.O.CO.C_{n'}H_{2n'+1}$$
$$+ (a - b)(C_nH_{2n+1}.OH + HO.CO.C_{n'}H_{2n'+1}).$$

By employment of an excess of alcohol an increased quantity of acid, by an excess of acid a larger quantity of alcohol, can be converted into the salt.

The yield of salt is increased by the presence of bodies which can combine with the resulting water, such as sulphuric acid or hydrochloric acid gas; but the action of these acids does not cease with combination with water, but, especially with sulphuric acid, they take part in the reaction, combining with the alcohol.

In preparing ethereal salts which volatilise unchanged, a mixture of alcohol and free acids or their salts is distilled after addition of sulphuric acid. The latter partly forms with the alcohol monalkyl sulphate, which at higher temperatures reacts with organic acids similarly to its reaction with alcohol and water (§ 215):

$$(C_nH_{2n+1})HSO_4 + HO.CO.C_{n'}H_{2n'+1} = \underset{\text{Ethereal salt.}}{C_nH_{2n+1}.O.CO.C_{n'}H_{2n'+1}}$$
$$+ H_2SO_4.$$

Volatile ethereal salts are also similarly obtained by the dry distillation of an intimate mixture of the alkali salts of fatty acids with potassic alkyl sulphates:

$$C_nH_{2n+1}KSO_4 + KO.C_{n'}H_{2n'-1}O = K_2SO_4$$
$$+ C_nH_{2n+1}O.C_{n'}H_{2n'-1}O.$$

The alcohols react very completely with acids when hydrochloric acid gas is passed to saturation into a mixture of the two. In the main the hydrochloric acid acts by uniting with the water, but also converts a portion of the alcohol into alkyl chloride, of which a certain quantity acts further as follows:

$$C_nH_{2n+1}.Cl + HO.CO.C_{n'}H_{2n'+1} = HCl + C_nH_{2n+1}.O.CO.C_n H_{2n'+1}.$$

This method is especially applicable when an insoluble salt of high boiling point is to be prepared from an alcohol miscible with water. After standing for several days the excess of alcohol is in great part distilled off, and the residue shaken with water. This removes alcohol and hydrochloric acid, whilst the ethereal salt separates and is purified either by distillation or, if solid, by crystallisation.

The following are also methods of general application:—

An alkyl haloid is heated with the potassic or argentic salt of the acid at 100°, best in the presence of some alcohol:

$$C_nH_{2n+1}Cl + KO.C_{n'}H_{2n'-1}O = KCl + C_nH_{2n+1}.O.C_{n'}H_{2n'-1}O.$$
$$C_nH_{2n+1}I + AgO.C_{n'}H_{2n'-1}O = AgI + C_nH_{2n+1}.O.C_{n'}H_{2n'-1}O.$$

The acid chlorides react with great energy on the alcohols yielding ethereal salts:

$$C_nH_{2n+1}.OH + Cl.CO.C_{n'}H_{2n'+1} = C_nH_{2n+1}.O.CO.C_{n'}H_{2n'+1} + HCl.$$

609. *Reactions of the Ethereal Salts.*—If not of very high molecular weight they are mostly liquids, distinguished, as a rule, from their constituent acids and alcohols by their agreeable odours. Many of them occur naturally, and impart to fruit, flowers, &c., their characteristic odour.

Solid crystalline ethereal salts of high molecular weight also occur naturally, forming the chief constituents of the various kinds of wax.

Treated with much water, and especially on heating, the ethereal salts are reconverted into acid and alcohol:

$$aC_nH_{2n+1}.O.C_{n'}H_{2n'-1}O + bH_2O = cC_nH_{2n+1}.OH + cHO.C_{n'}H_{2n'-1}O$$
$$+ (a-c)C_nH_{2n+1}O.C_{n'}H_{2n'-1}O + (b-c)H_2O;$$

the reaction being effected more readily and completely on heating with strong bases:

$$C_nH_{2n+1}O.C_nH_{2n-1}O + KOH = KO.C_{n'}H_{2n'-1}O + C_nH_{2n+1}OH.$$

As already mentioned, this process is termed *saponification.*

Ammonia, even in the presence of water, converts them into alcohol and acid amide:

$$C_nH_{2n+1}O.CO.C_{n'}H_{2n'+1} + NH_3 = C_nH_{2n+1}.OH$$
$$+ NH_2.CO.C_{n'}H_{2n'+1}.$$

Phosphoric chloride decomposes the ethereal salts into alkyl chlorides and acid chlorides:

$$C_nH_{2n+1}.O.C_{n'}H_{2n'-1}O + PCl_5 = POCl_3 + C_nH_{2n+1}Cl$$
$$+ ClC_{n'}H_{2n'-1}O.$$

By action of bromine and chlorine, substitution products are formed (with elimination of hydro-acids), in which even all the hydrogen atoms can be replaced by halogen. For this complete replacement the assistance of light and heat is requisite.

Ethereal Salts of the Mon-hydric Alcohols.

610. A very large number of cases of metamerism occur amongst the salts of this group, depending on the nature of the alcohols and acids. In addition to this they are further metameric with the monobasic acids, the general formula of the ethereal salts being the same as that of the fatty acids, $C_nH_{2n}O_2$:

$$C_{n'}H_{2n'+1}.O.CO.C_{n''}H_{2n''+1} = C_{n'+n''+1}H_{2(n'+n''+1)}O_2$$
$$= C_nH_{2n}O_2 \text{ if } n = n'+n''+1.$$

In comparison with the metameric acids the ethers always boil at lower temperatures and are less soluble in water. These liquids mix with alcohol and ether in every proportion.

611. *Methylic formate*, $CH_3.O.CHO$, metameric with acetic acid, is best obtained by distillation of sodic formate with potassic methyl sulphate. It is a mobile, colourless liquid, boiling at 36°.

612. $C_3H_6O_2$. *Ethylic formate*, $C_2H_5O.CHO$, is obtained by distillation of seven parts of dried sodic formate with six parts of 90 % alcohol and ten parts of sulphuric acid, or better by heating glycerine with oxalic acid and alcohol in a vessel provided with an inverted condenser (comp. § 567). It boils at 55° and dissolves in ten times its weight of water.

Methylic acetate, $CH_3.O.CO.CH_3$, occurs ready formed in crude wood spirit. It boils at 56° and has sp. gr. ·956 at 0°. The first chlor substitution product is *methene aceto-chloride*, $Cl.CH_2.O.CO.CH_3$, an oil boiling at 115°–116°, which on heating with water is converted into acetic and hydrochloric acids and methylic aldehyde.

613. $C_4H_8O_2$. *Propylic formate*, $CH_3.CH_2.CH_2.O.CO.H$, boils at 82·5°–83°.

Ethylic acetate, $CH_3.CH_2.O.CO.CH_3$, is best prepared by distilling ten parts of sodic acetate with a mixture of fifteen parts of sulphuric acid and six parts of alcohol. In order to remove any alcohol from the distillate, it is shaken several times with small quantities of a saturated solution of common salt, and the acetate then separated and dried by distillation over calcic chloride.

Pure ethylic acetate is a clear thin liquid of refreshing odour, boiling at 72°–74° and dissolving in about eleven times its weight of water, the latter soon partially decomposing it into acid and alcohol. It has sp. gr. ·9068 at 15°.

On adding sodium to perfectly pure ethylic acetate it dissolves with heating and evolution of but little gas to a mixture of sodic ethylate and ethylic aceto-sod-acetate (see ketonic acids).

Methylic propionate is not known.

614. $C_5H_{10}O_2$. Of the numerous possible salts of this molecular formula (four butylic formates, two propylic acetates, ethylic propionate, and two methylic butyrates) the following have been sufficiently investigated :—

Propylic acetate, $CH_3.CH_2.CH_2.O.CO.CH_3$, is a colourless liquid, boiling at 103°, of sp. gr. ·899 at 15°.

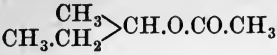
Isopropylic acetate, $(CH_3)_2:CH.O.CO.CH_3$, boils at 90°–92°.

Ethylic propionate, $C_2H_5.O.CO.C_2H_5$, boils at 99°–100° and has sp. gr. ·8945 at 17°.

Methylic butyrate, $CH_3.O.CO.CH_2.CH_2.CH_3$, boils at 93°, smells like butter, and has at 0° sp. gr. ·9091.

615. $C_6H_{12}O_2$. *Isoamylic formate*, $(CH_3)_2:CH.CH_2.CH_2.O.CHO$, boils at 112°, has sp. gr. ·8945 at 0°, and has an agreeable fruity odour.

Primary butylic acetate, $CH_3.CH_2.CH_2.CH_2.O.CO.CH_3$, boiling point 125°, sp. gr. ·8768 at 23°.

Secondary butylic acetate,  $\begin{matrix}CH_3\\CH_3.CH_2\end{matrix}>CH.O.CO.CH_3$, boils at 111°, sp. gr. ·892 at 0°.

Primary isobutylic acetate, $(CH_3)_2:CH.CH_2.O.C_2H_3O$, boils at 114°, sp. gr. ·8845 at 16°.

Tertiary isobutylic acetate, $(CH_3)_3.C.O.C_2H_3O$, boils at 96°.

Propylic propionate, $CH_3.CH_2.CH_2.O.CO.C_2H_5$, boils at 124·5°.

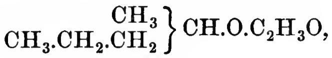
Ethylic butyrate, $C_2H_5.O.CO.CH_2.CH_2.CH_3$, is an oil boiling at 121°, of agreeable anise-like odour, and of sp. gr. ·9003 at 18°. *Ethylic isobutyrate*, $C_2H_5.O.CO.CH:(CH_3)_2$, boils at 113°.

Methylic isovalerate, $CH_3.O.CO.CH_2.CH:(CH_3)_2$, boils at 112°, sp. gr. ·896 at 0°.

616. $C_7H_{14}O_2$. *Normal primary amylic acetate :*

$$CH_3.CH_2.CH_2.CH_2.CH_2.O.C_2H_3O,$$

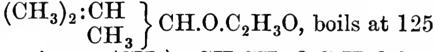
boils at 148·5°. *Normal secondary amylic acetate:*



$$\left.\begin{matrix}CH_3\\CH_3.CH_2.CH_2\end{matrix}\right\}CH.O.C_2H_3O,$$

boils at 140°. *Primary isoamylic acetate :*

$$(CH_3)_2:CH.CH.CH_2.O.C_2H_3O,$$

boils at 133°, and has the odour of jargonelle pears. *Secondary isoamylic acetate*,  $\left.\begin{matrix}(CH_3)_2:CH\\CH_3\end{matrix}\right\}CH.O.C_2H_3O$, boils at 125°.

Isobutylic propionate, $(CH_3)_2:CH.CH_2.O.C_3H_5O$, has boiling point 135·7°.

Isopropylic butyrate, $(CH_3)_2:CH.O.CO.CH_2.CH_2.CH_3$, boiling point 128°, sp. gr. ·878 at 0°.

Ethylic valerate, $C_2H_5.O.CO.CH_2.CH_2.CH_2.CH_3$, boils at 144·5° ; *ethylic isovalerate*, $C_2H_5.O.CO.CH_2.CH:(CH_3)_2$, at 133° ; and *ethylic trimethyl acetate*, $C_2H_5.O.CO.C:(CH_3)_3$, at 118·5°.

Methylic caproate, $CH_3.O.C_6H_{11}O$, has an unpleasant odour and boils at 131°.

617. $C_8H_{16}O$. The following are the best known salts of this formula :—

Hexylic acetate, $CH_3.CH_2.CH_2.CH_2.CH_2.CH_2.O.C_2H_3O$, an oil of agreeable fruity odour, boiling at 169°–170°.

Butylic butyrate, $CH_3.CH_2.CH_2.CH_2.O.CO.CH_2.CH_2.CH_3$, boils at 165·5°.

Isobutylic isobutyrate, $(CH_3)_2:CH.CH_2.O.CO.CH:(CH_3)_2$, boils at 142°, sp. gr. ·8702 at 0°.

Ethylic caproate, $C_2H_5.O.CO.CH_2.CH_2.CH_2.CH_2.CH_3$, boils at 167°.

Ethylic isocaproate, $C_2H_5.O.CO.CH_2.CH_2.CH:(CH_3)_2$, boils at 160·5°.

Ethylic dieth-acetate, $C_2H_5.O.CO.CH:(C_2H_5)_2$, boils at 151°.

618. $C_9H_{18}O_2$. *Ethylic œnanthate*, $C_2H_5.O.C_7H_{13}O$, is an oil of agreeable odour, boiling at 187°–188°, of sp. gr. ·8735 at 16°. The aroma of old wines appears to be in part due to this body.

$C_{10}H_{20}O_2$. *Hexylic butyrate*, $C_6H_{13}O.C_4H_7O$, and *octylic acetate*, $C_8H_{17}O.C_2H_3O$, form together that part of the oil of *Heracleum giganteum* which distils between 201° and 206°. The latter also forms the chief constituent of the oil of *Heracleum Spondylium* (§§ 171 and 173).

Isoamylic isovalerate, $(CH_3)_2:CH.CH_2.CH_2.O.CO.CH_2.CH:(CH_3)_2$, is formed as a bye product in the oxidation of fermentation amylic alcohol to isovaleric acid. It boils at 188° and smells agreeably like apples.

Ethylic caprylate, $C_2H_5.O.C_8H_{15}O$, also boils at 188°.

$C_{11}H_{22}O_2$. *Ethylic pelargonate*, $C_2H_5.O.C_9H_{17}O$, smells like *Pelargonium roseum*, boils at 207° and has sp. gr. ·86.

$C_{12}H_{24}O_2$. *Normal hexylic caproate*, $C_6H_{13}.O.C_6H_{11}O$, is obtained in the oxidation of normal primary hexylic alcohol as an oil of faint odour, boiling at 245·5°, and of sp. gr. ·865.

Ethylic caproate, $C_2H_5.O.C_{10}H_{19}O$, boils at 226°, sp. gr. ·862.

$C_{14}H_{28}O_2$. *Ethylic laurate*, $C_2H_5.O.C_{12}H_{23}O$, obtained by the action of hydrochloric acid on a solution of lauric acid in alcohol, boils at 264° and solidifies in crystals on cooling.

$C_{16}H_{32}O$. *Ethylic myristate*, $C_2H_5.O.C_{14}H_{27}O$, is an easily fusible, colourless, crystalline mass. *Normal caprylic octylate*, $C_8H_{17}O.C_8H_{15}O$, boils at 297°–299°, has sp. gr. ·8625.

619. The ethylic salts of the acids richer in carbon are all prepared by saturation of their alcoholic solutions with hydrochloric acid; they are crystallisable, wax-like, brilliant, colourless masses.

Ethylic palmitate, $C_2H_5.O.C_{16}H_{31}O$, melts at 24·2°; *ethylic stearate*, $C_2H_5.O.C_{18}H_{35}O$, at 33·7°; *ethylic arachidate*, $C_2H_5.O.C_{20}H_{39}O$, at 50°; and *ethylic cerotate*, $C_2H_5.O.C_{27}H_{53}O$, at 59°–60°.

Cetylic acetate, isomeric with ethylic palmitate, is obtained by saturation of a solution of cetylic alcohol in glacial acetic acid with hydrochloric acid. It crystallises in needles melting at 18·5°.

620. The highest members of this series form the chief constituents of vegetable and animal wax.

Cetylic palmitate, $C_{16}H_{33}.O.C_{16}H_{31}O$. Spermaceti consists in great part of this substance. It is obtained by crystallisation and pressing from the oil occurring in the bones of the skull of certain species of whales (*Physeter macrocephalus* and *Delphinus*), and forms a colourless mass of leafy crystals of waxy lustre. In the pure state it melts at 49°.

Bees'-wax is a mixture of several bodies, which are partially soluble (chiefly cerotic acid), partially insoluble in boiling alcohol. The chief ingredient of this latter portion is *mellissylic palmitate*, $C_{30}H_{61}.O.C_{16}H_{31}O$ (comp. § 179).

Chinese wax, a body of leafy crystalline fracture, consists of *cerylic cerotate*, $C_{27}H_{55}.O.C_{27}H_{53}O$.

A variety of wax is obtained by extracting meadow hay with hot alcohol; it consists of *mellissylic mellissate*:

$$C_{60}H_{120}O_2 = C_{30}H_{61}O.C_{30}H_{59}O.$$

Wax-like substances are widely diffused in plants—e.g. on the surface of green leaves, stalks, and many fruits (pears, apples, cherries, &c.) These still require investigation.

Salts of the Fatty Acids with the Diad Radicals, C_nH_{2n}.

621. *Alkylidene Salts.*—The more important of these compounds have already been mentioned, more especially the formation and properties of *methene diacetate*, $CH_2:(O.C_2H_3O)_2$ (§ 389); *ethylidene diacetate*, $CH_3.CH:(O.C_2H_3O)_2$, boiling point 169° (§ 393); and *ethylidene aceto-chloride*, $CH_3.CHCl.O.C_2H_3O$, boiling at 120°–124°.

622. The *salts of the olefines* have already been mentioned as intermediate products between the olefine haloids and the glycols. In their formation and decomposition they resemble the salts of the alkyls, but from the diad nature of their radicals exhibit some modification, especially in the methods of preparation.

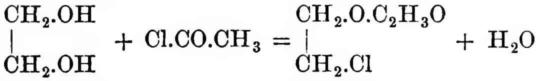
On heating a glycol with a fatty acid, a *basic* salt is first obtained:

$$C_nH_{2n}(OH).O.C_{n'}H_{2n'-1}O,$$

for whose conversion into the neutral salt a considerably higher temperature and excess of acid is requisite.

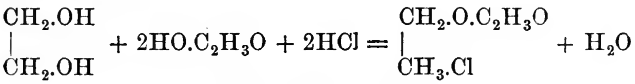
In the reaction between olefine dihaloids and salts of the fatty acids, normal ethereal salts only are formed, when the free acid itself is also present. If, on the other hand, alcohol be employed as a solvent, only basic salts of the olefine and alkyl salts are formed (§ 483).

On adding acidoxyl chlorides to the glycols, an energetic reaction ensues, whose chief product is an olefine chloro salt:



$$\begin{array}{l}CH_2.OH\\ |\\ CH_2.OH\end{array} + Cl.CO.CH_3 = \begin{array}{l}CH_2.O.C_2H_3O\\ |\\ CH_2.Cl\end{array} + H_2O$$

The same product is also formed in considerable quantity when hydrochloric acid gas is passed into a mixture of a glycol with an excess of an organic acid:



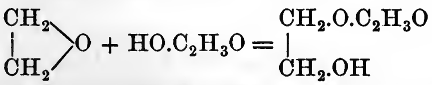
$$\begin{array}{l}CH_2.OH\\ |\\ CH_2.OH\end{array} + 2HO.C_2H_3O + 2HCl = \begin{array}{l}CH_2.O.C_2H_3O\\ |\\ CH_3.Cl\end{array} + H_2O$$

$$+ HO.C_2H_3O + HCl.$$

Acid anhydrides yield either basic or normal salts with the glycols, according to the proportions of the ingredients employed:

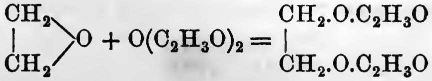
$$C_nH_{2n}(OH)_2 + (C_{n'}H_{2n'-1}O)_2O = C_nH_{2n}(OH).O.C_{n'}H_{2n'-1}O$$
$$+ HO.C_{n'}H_{2n'-1}O$$
$$C_nH_{2n}(OH)_2 + 2(C_{n'}H_{2n'-1}O)_2O = C_nH_{2n}(O.C_{n'}H_{2n'-1}O)_2$$
$$+ 2HO.C_{n'}H_{2n'-1}O.$$

Whilst the ethers or dialkyl oxides scarcely react with organic acids, the olefine oxides readily combine with them, forming basic salts:



$$\begin{array}{l}CH_2\\ |\\ CH_2\end{array}\!\!\Big\rangle O + HO.C_2H_3O = \begin{array}{l}CH_2.O.C_2H_3O\\ |\\ CH_2.OH\end{array}$$

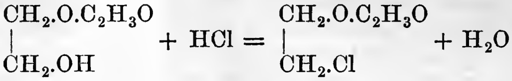
and with equal readiness with the anhydrides forming the normal salts:



$$\begin{array}{l}CH_2\\ |\\ CH_2\end{array}\!\!\Big\rangle O + O(C_2H_3O)_2 = \begin{array}{l}CH_2.O.C_2H_3O\\ |\\ CH_2.O.C_2H_3O\end{array}$$

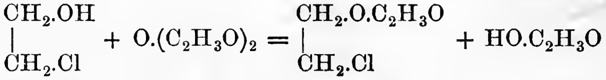
623. The acetates are best known of these compounds. A short notice of the characteristics of some few members will suffice.

Ethylene hydrate acetate is a liquid miscible with water, boiling at 182°. *Ethylene diacetate* requires seven times its weight of water for solution, and boils at 186°. *Ethylene aceto-chloride* is readily prepared by action of hydrochloric acid gas on the basic acetate:



$$\begin{array}{l} CH_2.O.C_2H_3O \\ | \\ CH_2.OH \end{array} + HCl = \begin{array}{l} CH_2.O.C_2H_3O \\ | \\ CH_2.Cl \end{array} + H_2O$$

and by heating ethylene hydrate chloride with acetic anhydride to 110°:



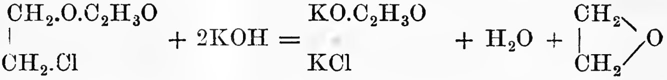
$$\begin{array}{l} CH_2.OH \\ | \\ CH_2.Cl \end{array} + O.(C_2H_3O)_2 = \begin{array}{l} CH_2.O.C_2H_3O \\ | \\ CH_2.Cl \end{array} + HO.C_2H_3O$$

it is isomeric with ethylidene aceto-chloride, and boils at 195°.

The basic salt yields with hydrobromic acid gas *ethylene bromoacetate*, $Br.CH_2.CH_2.O.C_2H_3O$, and with hydriodic acid *ethylene aceto-iodide*, which cannot be distilled without decomposition, and which is readily converted into ethylic acetate by excess of hydriodic acid:

$$I.CH_2.CH_2.O.C_2H_3O + HI = I_2 + CH_3.CH_2\,O.C_2H_3O.$$

The three haloid acetates of ethylene are liquids which sink in water, and on saponification yield ethylene oxide:



$$\begin{array}{l} CH_2.O.C_2H_3O \\ | \\ CH_2.Cl \end{array} + 2KOH = \begin{array}{l} KO.C_2H_3O \\ \\ KCl \end{array} + H_2O + \begin{array}{l} CH_2 \\ | \\ CH_2 \end{array}\!\!>O$$

The following basic ethylene salts are also known:—*Ethylene hydrate butyrate*, $C_2H_4(OH).O.C_4H_7O$, boiling point 220°; the *isovalerate*, $C_2H_4(OH).O.C_5H_9O$, boiling point about 240°. The neutral *butyrate*, $C_2H_4(O.C_4H_7O)_2$, boiling at 240°; the neutral *isovalerate*, boiling at 255°. Double salts are also known, such as *ethylene aceto-butyrate*, $C_2H_4(O.C_2H_3O)(O.C_4H_7O)$, boiling at 208°–215°, and the *aceto-isovalerate*, $C_2H_4(O.C_2H_3O)(O.C_5H_9O)$, boiling point about 230°. All the above neutral salts are oily liquids. *Ethylene distearate*, $C_2H_4(O.C_{18}H_{35}O)_2$, is solid and crystallises in plates which melt at 76°.

Acetates of the polyethylenic glycols (§ 506) are also known. Of the salts of higher members of the series there may be mentioned—

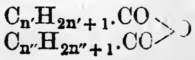
Propylene diacetate, $CH_3.CH(O.C_2H_3O).CH_2.(O.C_2H_3O)$, boils at 186°; the isomeric *trimethene diacetate*:

$$C_2H_3O.O.CH_2.CH_2.CH_2.O.C_2H_3O,$$

boils at 203°–205°. *Butylene diacetate* boils at 200°; *isoamylene diacetate*, at above 200°.

Anhydrides of the Fatty Acids.

624. If two oxygenated acid radicals are combined together by means of an oxygen atom, the anhydrides of monobasic acids result:



$$\begin{array}{l} C_{n'}H_{2n'+1}.CO \\ C_{n''}H_{2n''+1}.CO \end{array}\!\!>O$$

whose general molecular formula is $C_nH_{2n-2}O_3$. Their preparation is not effected directly from the acids, like the ethers from the alcohols, but is accomplished readily by the reaction of the acid haloids on anhydrous salt of the acids, the sodium salts being generally taken. The reaction is accompanied by considerable evolution of heat and separation of sodic chloride. If both the salt and acid haloid employed contain the same acid radical, the so-called *simple anhydrides* are formed:

$$C_{n'}H_{2n'+1}.CO.Cl + NaO.CO.C_{n'}H_{2n'+1} = NaCl \\ + C_{n'}H_{2n'+1}.CO.O.CO.C_{n'}H_{2n'+1},$$

whilst if derivatives of different acids be used, *mixed* anhydrides are obtained:

$$C_{n'}H_{2n'+1}.COCl + NaO.CO.C_{n''}H_{2n''+1} = NaCl \\ + C_{n'}H_{2n'+1}.CO.O.CO.C_{n''}H_{2n''+1}.$$

If the resulting anhydride can be volatilised unchanged, it is separated from the sodic chloride by distillation; in other cases the mixed product is extracted with ether, which dissolves the anhydride only and yields it again on evaporation.

In preparing the 'simple' anhydrides it is not necessary to first prepare the acid chloride, as the formation of this can be combined with its action on the salt into a single operation by decomposing four molecules of a salt with one molecule of phosphoric oxychloride (comp. § 603):

$$POCl_3 + 4NaO.C_nH_{2n-1}O = NaOPO_2 + 3NaCl + 2(C_nH_{2n-1}O)_2O.$$

625. The acid anhydrides are very unstable compounds in the presence of water or alcohol. At first they do not mix with water, but soon decompose with it into free acid:

$$(C_nH_{2n-1}O)_2O + OH_2 = 2C_nH_{2n-1}O.OH;$$

with alcohols they yield the free acid and ethereal salt:

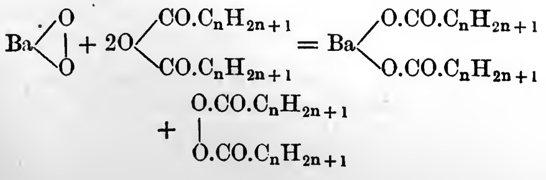
$$(C_nH_{2n-1}O)_2O + C_{n'}H_{2n'+1}.OH = C_{n'}H_{2n'+1}.O.C_nH_{2n-1}O \\ + C_nH_{2n-1}O.OH.$$

They are still more readily decomposed by basic oxides.

On heating with chlorine they yield acid chlorides and chlor substituted acids:

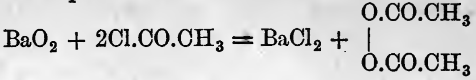
$$C_nH_{2n+1}.CO.O.CO.C_nH_{2n+1} + Cl_2 = C_nH_{2n+1}.COCl \\ + C_nH_{2n}Cl.CO.OH.$$

626. Baric peroxide converts the anhydrides into peroxides of the acid radicals, heat being evolved:



$$Ba\Big<\begin{matrix}O\\|\\O\end{matrix} + 2O\Big<\begin{matrix}CO.C_nH_{2n+1}\\CO.C_nH_{2n+1}\end{matrix} = Ba\Big<\begin{matrix}O.CO.C_nH_{2n+1}\\O.CO.C_nH_{2n+1}\end{matrix} \\ + \begin{matrix}O.CO.C_nH_{2n+1}\\|\\O.CO.C_nH_{2n+1}\end{matrix}$$

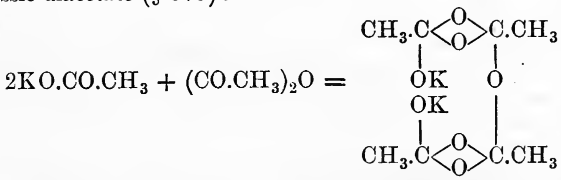
These latter compounds can also be obtained by action of acid chlorides on baric peroxide:



$$BaO_2 + 2Cl.CO.CH_3 = BaCl_2 + \begin{array}{l}O.CO.CH_3\\ |\\ O.CO.CH_3\end{array}$$

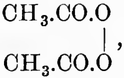
627. *Acetic anhydride, diacetyl oxide,* $C_4H_6O_3 = (CH_3.CO)_2O$, is obtained when one part of phosphoric oxychloride is allowed to slowly drop on three parts of finely powdered anhydrous sodic acetate, or when equal weights of acetic chloride and sodic acetate are similarly mixed. The reaction is conducted in a tubulated retort, and at its completion the acetic anhydride distilled.

It is a colourless, mobile liquid, of 1·073 sp. gr. at 20°, 138° boiling point, and 3·47 vapour density. It at first sinks in oily globules in pure water, but soon dissolves with evolution of heat and conversion into acetic acid. On heating with potassic acetate it dissolves two molecules of this salt, forming a crystalline compound corresponding to potassic diacetate (§ 575):



If chlorine gas be passed into acetic anhydride contained in a tubulated retort, and heated to 100°, chlor-acetyl distils, whilst monochlor acetic acid remains behind.

628. When baric peroxide is added to acetic anhydride mixed with ether, heat is evolved and baric acetate separates. The ethereal solution, decanted from the latter and evaporated, yields a residue of



Acetoxyl peroxide, $\begin{array}{l}CH_3.CO.O\\ \quad\quad\quad |\\ CH_3.CO.O\end{array}$, as a viscous liquid of persistent taste, not miscible with water. On slight heating it explodes with great violence. It decolorises indigo solution, liberates iodine from potassic iodide, and yields, with baric hydrate, baric acetate and baric peroxide:

$$(C_2H_3O)_2O_2 + 2Ba(OH)_2 = Ba(O.C_2H_3O)_2 + BaO_3H_2.$$

629. The other anhydrides resemble acetic anhydride so closely that a very short description will suffice.

Propionic anhydride, $(CH_3.CH_2.CO)_2O$, boils at 165°.

Butyric anhydride, $(CH_3.CH_2.CH_2.CO)_2O$, boiling point about 190°, sp. gr. ·978, vapour density 5·38 (calculated 5·44).

Isovaleric anhydride, $([CH_3]_2 : CH.CH_2.CO)_2O$, boils at 215°.

Caprylic anhydride, $(C_7H_{15}.CO)_2O$, solidifies in crystals at —18°, is liquid at 0°, and boils with partial decomposition between 180° and 190°.

Pelargonic anhydride, $(C_8H_{17}.CO)_2O$, solidifies at 0°, melts at + 5°, and cannot be distilled without decomposition.

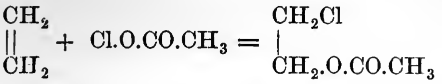
Myristic anhydride, $(C_{11}H_{23}.CO)_2O$, is a fatty mass which melts at 54°.

630. Some compounds may be mentioned here which are the mixed anhydrides of fatty and inorganic acids.

Aceto-hypochlorous anhydride, chlorine acetate, $CH_3.CO.Cl$, formed on strongly cooling acetic anhydride and chlorine monoxide :

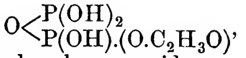
$$(C_2H_3O)_2O + Cl_2O = 2C_2H_3O.O.Cl,$$

as a colourless liquid, not miscible with water, which on heating to 100° explodes violently, and is decomposed by water into acetic and hypochlorous acids. It absorbs ethylene with formation of ethylene acetochloride :



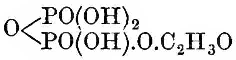
$$\begin{array}{l} CH_2 \\ \| \\ CH_2 \end{array} + Cl.O.CO.CH_3 = \begin{array}{l} CH_2Cl \\ | \\ CH_2.O.CO.CH_3 \end{array}$$

Aceto-iodous anhydride, or *iodine triacetate,* $I(O.CO.CH_3)_3$, is obtained, by passing chlorine monoxide into a solution of iodine in acetic anhydride, as colourless prisms, which explode between 100° and 140° and deliquesce in moist air.

Aceto-pyrophosphorous acid,  $O\begin{matrix}\diagup P(OH)_2 \\ \diagdown P(OH).(O.C_2H_3O)\end{matrix}$, is prepared by the action of acetic chloride on phosphorous acid :

$$2P(OH)_3 + 2ClC_2H_3O = 2HCl + HO.C_2H_3O + P_2(C_2H_3O)H_3O_5.$$

It yields dibasic salts with the metals, and in the case of lead a tribasic salt. On oxidation with hydric peroxide (baric peroxide in presence of hydrochloric acid) it yields the tribasic *aceto-pyrophosphoric acid :*



$$O\begin{matrix}\diagup PO(OH)_2 \\ \diagdown PO(OH).O.C_2H_3O\end{matrix}$$

Aceto-ortho-silicic anhydride, silicon tetracetate, $Si(O.C_2H_3O)_2$, is obtained on heating a mixture of one molecule of silicic tetrachloride and four molecules of acetic acid (with elimination of 4HCl), or with four molecules of acetic anhydride (together with $4Cl.CO.CH_3$). On cooling the compound crystallises in white quadratic prisms, melting at 110°, boiling at 148° under a pressure of 6 mm., but decomposing at 160°–170° into silica and acetic anhydrides :

$$Si(O.CO.CH_3)_4 = SiO_2 + 2O(CO.CH_3)_2.$$

Thio-Acids, their Salts and Anhydrides.

631. On adding liquid fatty acids to phosphorus tri- or pentasulphide, oxides of phosphorus and *thio-acids* are formed, with evolution of heat. The thio-acids can be purified by distillation :

$$P_2S_5 + 5HO.CO.C_nH_{2n+1} = P_2O_5 + 5HS.CO.C_nH_{2n+1}.$$

In similar manner the anhydrides and phosphorus sulphides yield thio-anhydrides—diacidoxyl sulphides :

$$P_2S_5 + 5O(CO.C_nH_{2n+1})_2 = P_2O_5 + 5S(CO.C_nH_{2n+1})_2.$$

Ethereal thio-salts are prepared from metallic mercaptides and acid chlorides :

$$C_nH_{2n+1}SK + Cl.CO.C_{n'}H_{2n'+1} = KCl + C_nH_{2n+1}.S.CO.C_{n'}H_{2n'+1},$$

or from alkyl haloids and metallic salts of thio-acids :

$$C_nH_{2n+1}I + NaS.CO.C_{n'}H_{2n'+1} = NaI + C_nH_{2n+1}.S.CO.C_{n'}H_{2n'+1}.$$

The ethereal oxy-salts can also be converted into thio-salts by action of phosphorus sulphides, but further decompositions readily ensue.

Thio-anhydrides are slowly converted by water into oxy- and thio-acids :

$$S(CO.C_{n'}H_{2n'+1})_2 + H_2O = HO.CO.C_{n'}H_{2n'+1} + HS.CO.C_{n'}H_{2n'+1}.$$

632. By action of nitric acid the sulphur of the thio compounds is oxidised, the thio-acids and anhydrides yielding sulphuric and fatty acids :

$$HS.CO.C_{n'}H_{2n'+1} + 4O + H_2O = H_2SO_4 + HO.CO.C_{n'}H_{2n'+1}$$
$$S(CO.C_{n'}H_{2n'+1})_2 + 4O + 2H_2O = H_2SO_4 + 2HO.CO.C_{n'}H_{2n'+1}.$$

The ethereal thio-salts yield the respective alkyl sulphonic acids and fatty acids :

$$C_nH_{2n+1}.S.CO.C_{n'}H_{2n'+1} + 3O + H_2O = C_nH_{2n+1}.SO_2.OH + HO.CO.C_{n'}H_{2n'+1}.$$

633. Thio derivatives of formic acid have not yet been prepared in the pure state. By the decomposition of plumbic formate by hydric sulphide there is formed—especially when the temperature is high (200°–300°)—a crystalline sulphuretted product, which was formerly taken for thio-formic acid, but later has been shown not to possess a definite composition.

634. *Acetoxyl Derivatives.—Thiacetic acid*, $CH_3.CO.SH$, is formed, in addition to the above-mentioned reactions, by the action of acetic chloride on potassic sulph-hydrate ; it is a colourless liquid, soon turns yellow, and has an odour resembling both acetic acid and hydric sulphide. It mixes in every proportion with alcohol and ether, but is more difficultly soluble in water. It boils at 93°, has at 10° sp. gr. 1·074, and does not solidify at $-17°$. Phosphoric pentachloride reacts on it as on acetic acid.

$$PCl_5 + HS.CO.CH_3 = PSCl_3 + HCl + Cl.CO.CH_3.$$

Its salts are mostly crystalline and readily soluble. *Plumbic thiacetate*, $Pb(S.CO.CH_3)_2$, forms characteristic colourless needles, which after some time blacken, with formation of plumbic sulphide and probably of sulphacetic anhydride.

Ethylic thiacetate, $C_2H_5.S.CO.CH_3$, is an oil which floats on water and boils at 117°.

Thiacetic anhydride, diacetoxyl sulphide, is a yellowish oil, which boils at 121°, at first sinks in water, and then slowly dissolves to acetic and thiacetic acids.

Diacetoxyl disulphide, $S_2(CO.CH_3)_2$, is formed according to the general method for obtaining disulphides (§ 242) by decomposing alkaline thiacetates with iodine :

$$2KS.CO.CH_3 + I_2 = 2KI + \begin{array}{l} S.CO.CH_3 \\ | \\ S.CO.CH_3 \end{array}$$

It is a yellow crystalline body, decomposed on distillation.

635. *Thiobutyric acid*, $CH_3.CH_2.CH_2.CO.SH$, is a liquid of nauseous odour, boils at 130°, and is nearly insoluble in water.

Nitrogen Compounds of the Acid Oxyls.

636. *Formation.*—The acid oxyls can be substituted for the hydrogen of ammonia in similar manner to the alcohol radicals, whereby first amide (NH_2) compounds, the *acid amides*, are formed. They are obtained by action of the acid haloids on ammonia :

$$C_nH_{2n+1}.CO.Cl + 2NH_3 = C_nH_{2n+1}.CO.NH_2 + NH_4Cl,$$

and can be separated from the accompanying ammonic salts by solution in anhydrous alcohol or ether.

They are prepared more conveniently from the ethereal salts of the fatty acids, which by long standing, or more quickly by heating with ammonia solution, are decomposed into alcohols and acid amides :

$$C_nH_{2n+1}.O.CO.C_{n'}H_{2n'+1} + NH_3 = C_nH_{2n+1}.OH + NH_2.CO.C_{n'}H_{2n'+1}$$

$$C_nH_{2n}(O.CO.C_{n'}H_{2n'+1})_2 + 2NH_3 = C_nH_{2n}(OH)_2 + 2NH_2.CO.C_{n'}H_{2n'+1}.$$

Those members of the series which can be distilled unchanged are usually prepared by dry distillation of the ammonic salts of the acids :

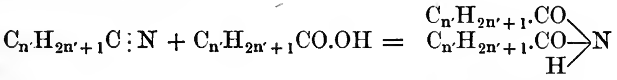
$$C_{n'}H_{2n'+1}.CO.O.NH_4 = H_2O + C_{n'}H_{2n+1}.CO.NH_2,$$

or, what comes to the same thing, by distillation of a dry mixture of the sodic salt of the fatty acid with ammonic chloride.

The anhydrides are decomposed by ammonia, yielding acid amides and ammonic salts :

$$O(CO.C_{n'}H_{2n'+1})_2 + 2NH_3 = NH_4.O.CO.C_{n'}H_{2n'+1} + NH_2.CO.C_{n'}H_{2n'+1}.$$

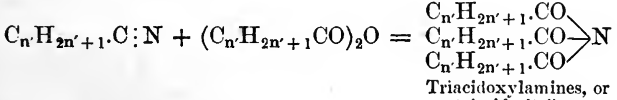
637. *Di-* and *triacid oxylamine* compounds cannot be obtained from the acid amides by a repetition of their method of formation, these bodies being only obtainable indirectly, as by heating the acid nitriles with the acids to 200° :



$$C_{n'}H_{2n'+1}C \vdots N + C_{n'}H_{2n'+1}CO.OH = \left.\begin{matrix} C_{n'}H_{2n'+1}.CO \\ C_{n'}H_{2n'+1}.CO \\ H \end{matrix}\right\rangle N$$

Diacidoxylamine, or diacid amide.

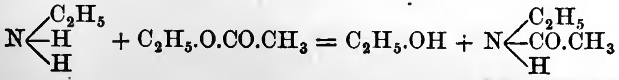
and with the anhydrides :



$$C_{n'}H_{2n'+1}.C \vdots N + (C_{n'}H_{2n'+1}CO)_2O = \left.\begin{matrix} C_{n'}H_{2n'+1}.CO \\ C_{n'}H_{2n'+1}.CO \\ C_{n'}H_{2n'+1}.CO \end{matrix}\right\rangle N$$

Triacidoxylamines, or triacid nitriles.

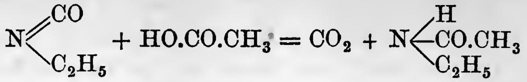
638. If, instead of ammonia, alkylamines are employed in the method of preparing acid amides, there are obtained *alkyl acidoxylamines*; e.g.



$$N\left\langle\begin{matrix} C_2H_5 \\ H \\ H \end{matrix}\right. + C_2H_5.O.CO.CH_3 = C_2H_5.OH + N\left\langle\begin{matrix} C_2H_5 \\ CO.CH_3 \\ H \end{matrix}\right.$$

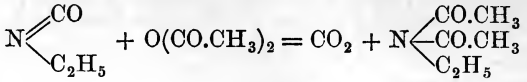
Ethyl acetamine.

The same compounds are obtained by action of ethereal isocyanates on fatty acids:



$$N\left\langle\begin{array}{l}CO\\ C_2H_5\end{array}\right. + HO.CO.CH_3 = CO_2 + N\left\langle\begin{array}{l}H\\ CO.CH_3\\ C_2H_5\end{array}\right.$$

whilst with anhydrides *diacid-oxyl alkylamines* are formed:



$$N\left\langle\begin{array}{l}CO\\ C_2H_5\end{array}\right. + O(CO.CH_3)_2 = CO_2 + N\left\langle\begin{array}{l}CO.CH_3\\ CO.CH_3\\ C_2H_5\end{array}\right.$$

Ethyl diacetamine.

639. In like manner to their action on ammonia, the acid chlorides also react on other ammonia derivatives in which there is still hydrogen united to nitrogen. The acid-oxyl group can thus be inserted in urea, sulph-urea, isocyanides, &c.; e.g.

$$NH_2.CO.NH_2 + Cl.CO.C_{n'}H_{2n'+1} = HCl$$
$$+ NH_2.CO.NH(CO.C_{n'}H_{2n'+1}).$$

Acid-oxyl urea.

$$C \vdots NAg + Cl.CO.CH_3 = AgCl + C \vdots N.CO.CH_3.$$

Isocyanacetoxyl.

640. *Properties.*—Whilst the alcohol radicals can only be separated with difficulty from the nitrogen united to them, the acid oxyls are readily disunited from their amide compounds, this occurring even by heating with water, which unites directly with the monamides, forming ammonic salts:

$$C_{n'}H_{2n'+1}.CO.NH_2 + H_2O = C_{n'}H_{2n'+1}.CO.O.NH_4;$$

more readily by means of alkalies:

$$C_{n'}H_{2n'+1}.CO.NH_2 + HOK = C_{n'}H_{2n'+1}CO.OK + NH_3,$$

or by acids in presence of water:

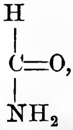
$$C_nH_{2n+1}.CO.NH_2 + H_2O + HCl = NH_4Cl + C_{n'}H_{2n'+1}.CO.OH.$$

Nitrous acid readily oxidises them, with liberation of nitrogen:

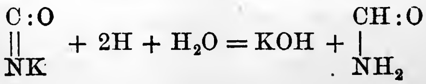
$$C_{n'}H_{2n'+1}.CO.NH_2 + HO.NO = H_2O + N_2 + C_{n'}H_{2n'+1}.CO.OH.$$

The formation of acid nitriles or alkyl cyanides by heating the acid amides with phosphoric anhydride has been already mentioned (§ 545).

Formoxyl Compounds.



641. *Formyl amide*, or *formamide*, $CH_3NO = \begin{array}{c}H\\ |\\ C{=}O\\ |\\ NH_2\end{array}$, is formed by heating ethereal formates to 100° with alcoholic ammonia, and by the dry distillation of ammonic formate; also by the action of nascent hydrogen on potassic isocyanate:



$$\begin{array}{c}C:O\\ \|\\ NK\end{array} + 2H + H_2O = KOH + \begin{array}{l}CH:O\\ |\\ NH_2\end{array}$$

It is a colourless liquid, readily soluble in water and alcohol, which boils at 192°–195°, partially decomposing into carbonic oxide and ammonia:

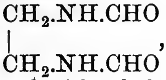
$$CHO.NH_2 = CO + NH_3.$$

Phosphoric anhydride converts it into prussic acid (formo-nitrile):

$$CHO.NH_2 + P_2O_5 = 2HPO_3 + CHN.$$

Ethyl form-amide, $N(C_2H_5)(CHO)H$, is obtained by the decomposition of ethereal formates by ethylamine, as also, together with chloroform, by distillation of a mixture of chloral and ethylamine.

It is a liquid which boils at 199°.

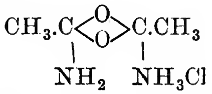
Ethylene diform-amide,  $\begin{matrix} CH_2.NH.CHO \\ | \\ CH_2.NH.CHO \end{matrix}$, is obtained as a transparent syrup on heating chloral with ethylene diamine:

$$C_2H_4:(NH_2)_2 + 2CCl_3.CHO = C_2H_4:(NH.CHO)_2 + 2CHCl_3.$$

Alkalies convert it into an alkaline formate and ethylene diamine, acids into formic acid and a salt of ethylene diamine.

Acetoxyl Compounds.

642. *Acetamide*, $C_2H_5NO = CH_3.CO.NH_2$, is obtained by heating ethereal acetates with ammonia to 100°–120°, by the dry distillation of ammonic acetate, and other general methods. It forms long colourless needles, which smell like the excrements of mice, melt at 78°–79°, and distil at 222°. It is readily soluble in alcohol, difficultly in ether. It yields weak compounds with acids which are decomposed by water. On passing hydrochloric acid into an ethereal solution of acetamide, lanceolate crystals separate of the formula $2C_2H_5NO,HCl$, or



$$\begin{matrix} CH_3.C\!\!<\!\!\overset{O}{\underset{O}{}}\!\!>\!\!C.CH_3 \\ \quad | \qquad\qquad | \\ NH_2 \qquad NH_3Cl \end{matrix} \qquad \text{acetamide hydrochloride,}$$

which on heating decomposes partially into acetyl diamine hydrochloride (§ 554), and acetic acid, partly into ammonic chloride and diacetoxylamine:

$$(CH_3.CO.NH_2)_2HCl = NH_4Cl + (CH_3.CO)_2NH.$$

A solution of acetamide in concentrated nitric acid yields, on evaporation of the excess of acid, leafy crystals of *acetamide nitrate:*

$$N(CO.CH_3)H_3.O.NO_2.$$

On boiling an acetamide solution with mercuric oxide, and evaporating the filtered liquid, colourless crystals of *mercuric acetamide:*

$$Hg[N(C_2H_3O)H]_2,$$

are obtained.

Ethyl acetamide, $N(C_2H_5)(C_2H_3O)H$, is obtained on decomposing ethylic acetate with ethylamine, and by action of acetic acid on ethylic isocyanate. It is a syrup boiling at 200°.

643. *Diacetamide*, or *diacetylamine*, $N(CO.CH_3)_2H$, is obtained by heating acetamide with hydrochloric acid, or aceto-nitrile with acetic acid, at 200°. It forms colourless crystals, readily soluble in water, melts at 59°, and boils at 210°–215°.

Ethyl diacetamide, $N(C_2H_5)(CO.CH_3)_2$, is formed on bringing together ethylic isocyanate and acetic anhydride :

$$OC{=}N.C_2H_5 + O(CO.CH_3)_2 = CO_2 + N.C_2H_5.(CO.CH_3)_2.$$

644. *Triacetamide*, or *triacetylamine*, $N(CO.CH_3)_3$, is formed by heating a mixture of aceto-nitrile with acetic anhydride to 200° :

$$N \vdots C.CH_3 + O(CO.CH_3)_2 = N(CO.CH_3)_3.$$

It forms small colourless crystals, melting at 78°–79°.

645. *Acetyl urea*, $NH_2.CO.N(CO.CH_3)H$. If acetic chloride is poured over urea, the mass becomes heated, with evolution of hydrochloric acid and formation of acetyl urea. The same compound is also formed, together with acetic acid, by the action of acetic anhydride on urea.

Acetyl urea crystallises in long needles, little soluble in cold water, melting at 112°, and decomposing at higher temperatures in cyanuric acid and acetamide, similarly to the conversion of urea into cyanuric acid and ammonia. Acetyl urea does not yield compounds with acids.

On heating carbonic oxychloride with acetamide to 50°, *diacetyl urea* is formed :

$$COCl_2 + 2N(C_2H_3O)H_2 = 2HCl + CO(N.C_2H_3O.H)_2.$$

The hydrochloric acid so formed reacts in turn on the acetamide, so that aceto-nitrile, water, acetic acid, and ammonic chloride are also formed. Diacetyl urea crystallises in colourless needles, which are difficultly soluble in cold water and can be sublimed without decomposition.

Acetyl sulph-urea, $NH_2.CS.NH(C_2H_3O)$, is readily prepared from sulph-urea by action of acetic chloride or acetic anhydride. It crystallises in colourless prisms, which melt at 165° and dissolve in large quantity in water and alcohol.

646. *Acetic isocyanide, cyanacetyl*, is obtained by the action of acetic chloride on argentic cyanide :

$$CH_3.CO.Cl + Ag.N \vdots C = AgCl + CH_3.CO.N \vdots C.$$

It is a liquid boiling at 93°, which is decomposed by water into acetic and hydrocyanic acids, and by warming with aqueous acids into acetic and formic acids and ammonic salts :

$$CH_3.CO.N \vdots C + 3H_2O + HCl = CH_3.CO.OH \\ + NH_4Cl + CHO.OH ;$$

and on long standing, or by contact with sodium, is converted into a crystalline polymeric compound, melting at 69° and boiling at 208°–209°.

647. *Propionamide*, $CH_3.CH_2.CO.NH_2$, crystallises in colourless prisms, melting at 75°–76° and boiling above 210°.

Butyramide, $CH_3.CH_2.CH_2.CO.NH_2$, melts at 115°, boils at 216°.

Isobutyramide, $(CH_3)_2 : CH.CO.NH_2$ (§ 549), forms crystals of agreeable odour, melting at 100°–102°.

Isovaleramide, $(CH_3)_2:CH.CH_2.CO.NH_2$, crystallises in leafy crystals.

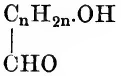
Amides of acids richer in carbon have been prepared by decomposition of the ethereal salts with ammonia. Their melting points are as follows: *œnanthamide*, $C_6H_{13}.CO.NH_2$, at 95°; *caprylamide*, $C_7H_{15}.CO.NH_2$, at 110°; *palmitamide*, $C_{15}H_{31}.CO.NH_2$, at 93·5°.

Mixtures of several amides are obtained by shaking the fats, the glyceric salts of fatty acids, with aqueous or alcoholic ammonia:

$$C_3H_5.(O.C_nH_{2n-1}O)_3 + 3NH_3 = C_3H_5(OH)_3 + 3NH_2.C_nH_{2n-1}O.$$

DERIVATIVES OF THE ALDEHYDE ALCOHOL RADICALS, $\begin{array}{l} C_{n'}H_{2n'}— \\ | \\ CH= \end{array}$

648. If in a paraffin three hydrogen atoms have been so replaced by oxygen that on one terminal carbon atom two, on another only one substitution position occurs, the body formed in the simplest case of oxygen union will be:

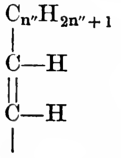


$$\begin{array}{l} C_nH_{2n}.OH \\ | \\ CHO \end{array}$$

which is at the same time aldehyde and alcohol.

Only few of the derivatives of their triad hydrocarbon radicals, the *alkenyls*, are known, and these are mostly halogen compounds.

When the substitution positions are neighbouring, double union can occur between the carbon atoms. The nuclei:



$$\begin{array}{l} C_{n''}H_{2n''+1} \\ | \\ C—H \\ \| \\ C—H \\ | \end{array}$$

are then united with monad elements or radicals, and have the character of 'unsaturated' compounds—i.e. can combine directly with two halogen atoms, like the olefines, as whose first substitution products they appear.

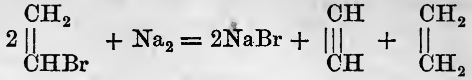
Ethenyl Compounds.

649. The radical $C_2H_3 = CH_2:CH.$ is termed *vinyl.*

Vinylic chloride, monochlor ethylene, $CH_2:CHCl$, is obtained from ethylenic dichloride by action of alcoholic potassic hydrate (§ 473), as also, though with more difficulty, from ethylidenic chloride, as a colourless gas of garlic odour, which on strong cooling is condensed to a liquid boiling at −18°:

$$CH_2.Cl.CH_2Cl + KOH = KCl + H_2O + CH_2:CHCl$$
$$CH_3.CHCl_2 + KOH = KCl + H_2O + CH_2:CHCl.$$

Vinylic bromide, monobrom ethylene, $CH_2:CHBr$, prepared similarly to the foregoing from ethylene dibromide (§ 474), is a liquid not miscible with water, of boiling point 23°. Sodium converts it into a mixture of ethylene and acetylene:



$$2\begin{matrix}CH_2\\ \|\\ CHBr\end{matrix} + Na_2 = 2NaBr + \begin{matrix}CH\\ |||\\ CH\end{matrix} + \begin{matrix}CH_2\\ \|\\ CH_2\end{matrix}$$

Vinylic iodide, moniod-ethylene, boils at 55° and has sp. gr. 1·98 (§ 475).

All three vinylic haloids are converted into acetylene when heated with alcoholic potassic hydrate.

The formation and properties of the nitrogen and phosphorus bases have been already mentioned (§ 523).

650. *Ethenyl trihaloids* are formed from the vinylic haloids by direct combination with halogens.

Ethenyl trichloride, chlor-ethylene dichloride, $CH_2Cl.CHCl_2$, is a colourless oil boiling at 115°, and having sp. gr. 1·4223 at 0°.

Ethenyl tribromide, brom-ethylene dibromide, $CH_2Br.CHBr_2$, smells like chloroform, and does not mix with water; it boils at 186·5° and has sp. gr. 2·62 at 23°.

Ethenyl dichloride ethylate, $CH_2Cl.CHCl.O.C_2H_5$, is the *bichlor ether* obtained by the direct action of chlorine on ether (§ 207). To prepare it, perfectly pure ether is placed in a flask cooled with ice, and chlorine passed into it. When the liquid, coloured green by chlorine, is only slowly decolorised, it is distilled from the water bath, when ether distils over. The brown residue is then submitted to fractional distillation, that passing over between 140°–147° being bichlor ether, which is purified by renewed fractionation.

Bichlor ether is a colourless liquid, of sp. gr. 1·174 at 23°, and boils with slight decomposition at 145°. It dissolves slowly in water, yielding hydrochloric acid, alcohol, and apparently aldehyde-like bodies. For its conversion into ethyl chlor-ether and secondary normal butylic alcohol see § 169, 2.

Ethenyl chloride diethylate, $CH_2Cl.CH(O.C_2H_5)_2$, *chlor-acetal*, is formed, together with further substitution products, by the action of chlorine on 80 % alcohol:

$$CH_3.CH_2.OH + 2HO.C_2H_5 + 2Cl_2 = CH_2Cl.CH(OC_2H_5)_2 + H_2O + 3HCl.$$

It is also formed by slowly adding sodium ethylate to bichlor ether:

$$CH_2Cl.CHCl(O.C_2H_5) + NaO.C_2H_5 = NaCl + CH_2Cl.CH(OC_2H_5)_2,$$

and rectifying the oil separated by water. It boils at 157°, has sp. gr. about 1·02, and is not altered by potassic hydrate.

Ethenyl bromide diethylate, $CH_2Br.CH(O.C_2H_5)_2$, *brom-acetal*, is formed by dropping bromine into cooled acetal. It is a heavy, colourless oil, boiling with partial decomposition at 170°.

651. A very violent reaction occurs between bichlor ether and concentrated solution of potassic hydrate; an oily liquid separates, which can be resolved into two compounds by repeated fractional distillation.

Ethenyl hydrate ethylate chloride, or *β-oxychlor ether:*

$$CH_2(OH).CHCl.O.C_2H_5,$$

boils between 151° and 155°.

Ethenyl chloride ethylate oxide, $[CH_2Cl.CH(OC_2H_5)]_2O$, boils at 163°–165°. This latter body results from the decomposition of the substance next to be described.

Ethenyl chloride ethylate hydrate, *a*-oxychlor ether, or *monochlor aldehyde alcoholate*, $CH_2Cl.CH(OH)(O.C_2H_5)$, is obtained by the action of water at high temperatures on bichlor ether, as a liquid boiling at between 95°–96° :

$$CH_2Cl.CHCl(O.C_2H_5) + HOH = HCl + CH_2Cl.CH(OH)(O.C_2H_5).$$

On repeated distillation it decomposes slowly into ethenyl chloride ethylate oxide and water. The reaction of potassic hydrate on bichlor ether is represented by the equation :

$$aCH_2Cl.CHCl(O.C_2H_5) + aKOH = aKCl$$
$$+ bCH_2(OH).CHCl.(OC_2H_5) + (a-b)CH_2Cl.CH(OH)(O.C_2H_5).$$

652. *Monochlor aldehyde*, or *ethenyl chloride oxide*, is obtained by gently heating chlor-acetal or ethenyl chloride ethylate hydrate with concentrated sulphuric acid :

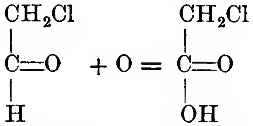
$$CH_2Cl.CH(OH)(O.C_2H_5) + H_2SO_4 = C_2H_5.HSO_4 + H_2O$$
$$+ CH_2Cl.CHO\,;$$

it is also obtained from vinylic chloride by oxidation with hypochlorous acid :

$$CHCl : CH_2 + HOCl = CH_2Cl.CHO + HCl.$$

In presence of water monochlor aldehyde can be distilled below 100°, probably as ethenyl chloride dihydrate, $CHCl.CH(OH)_2$.

It oxidises in the air and reduces argentic oxide, being converted into chloracetic acid :

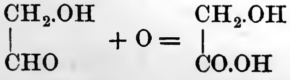


$$\begin{array}{c} CH_2Cl \\ | \\ C{=}O \\ | \\ H \end{array} + O = \begin{array}{c} CH_2Cl \\ | \\ C{=}O \\ | \\ OH \end{array}$$

653. *Oxyaldehyde*, or ethenyl hydrate oxide, $CH_2(OH).CHO$, has not yet been obtained in a state of purity, but is formed in some quantity when bichlor ether is heated with water, or β-oxychlor ether with strong sulphuric acid :

$$CH_2Cl.CHCl.O.C_2H_5 + 2H_2O = CH_2(OH).CHO + 2HCl$$
$$+ HO.C_2H_5$$
$$CH_2(OH).CHCl(O.C_2H_5) + H_2SO_4 = CH_2(OH).CHO + HCl$$
$$+ C_2H_5.HSO_4.$$

On shaking the brown mass obtained in the latter case with ether, and evaporating the ethereal solution, there is obtained a syrup of persistent aldehyde-like odour, which oxidises to glycollic acid on exposure to air, or more quickly by treatment with argentic oxide :

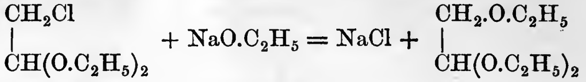


$$\begin{array}{c} CH_2.OH \\ | \\ CHO \end{array} + O = \begin{array}{c} CH_2.OH \\ | \\ CO.OH \end{array}$$

Oxyaldehyde. Glycollic acid.

Oxyacetal, or *glycol acetal*, $CH_2.(OH).CH(O.C_2H_5)_2$, ethenyl hydrate diethylate, is obtained by heating brom-acetal with potassic hydrate to 160°. It is a liquid of agreeable odour, boiling at 167°.

654. *Ethenyl triethylate*, $CH_2(OC_2H_5).CH(OC_2H_5)_2$, is formed by heating chlor-acetal with sodic ethylate to 140°–150° :



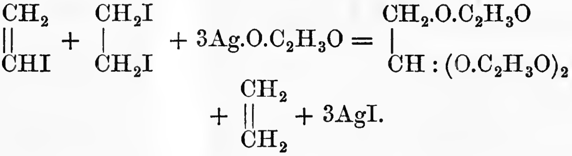
$$\begin{array}{l}CH_2Cl\\ |\\ CH(O.C_2H_5)_2\end{array} + NaO.C_2H_5 = NaCl + \begin{array}{l}CH_2.O.C_2H_5\\ |\\ CH(O.C_2H_5)_2\end{array}$$

On addition of water it separates as an oil boiling at 168°, of sp. gr ·8924 and vapour density 5·8.

Ethenyl triacetate, $CH_2(O.C_2H_3O).CH(O.C_2H_3O)_2$, is obtained in small quantity, together with ethylene diacetate, when ethylenic diiodide is heated with argentic acetate and glacial acetic acid. Vinylic iodide is first formed, HI being evolved :

$$CH_2I.CH_2I + AgO.C_2H_3O = AgI + HO.C_2H_3O + CH_2 : CHI$$

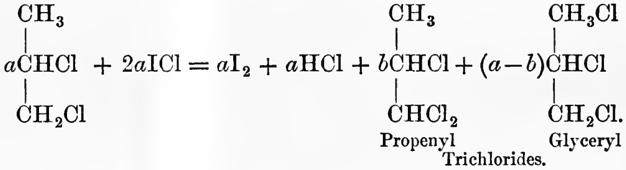
which then further reacts as in the following equation :



$$\begin{array}{l}CH_2\\ \|\\ CHI\end{array} + \begin{array}{l}CH_2I\\ |\\ CH_2I\end{array} + 3Ag.O.C_2H_3O = \begin{array}{l}CH_2.O.C_2H_3O\\ |\\ CH : (O.C_2H_3O)_2\end{array} + \begin{array}{l}CH_2\\ \|\\ CH_2\end{array} + 3AgI.$$

Ethenyl triacetate boils somewhat above 250°.

655. *Propenyl trichloride*, $CH_3.CHCl.CHCl_2$, is formed, together with glyceryl trichloride, by the action of iodine chloride on propylene dichloride at 170° :

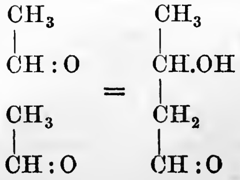


$$\begin{array}{l}CH_3\\ |\\ aCHCl\\ |\\ CH_2Cl\end{array} + 2aICl = aI_2 + aHCl + \begin{array}{l}CH_3\\ |\\ bCHCl\\ |\\ CHCl_2\end{array} + (a-b)\begin{array}{l}CH_2Cl\\ |\\ CHCl\\ |\\ CH_2Cl.\end{array}$$

Propylene trichloride is a colourless oil, distilling between 138° and 140°.

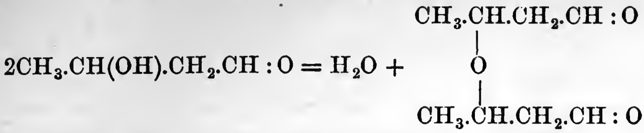
656. *Aldol*, $CH_3.CH(OH).CH_2.CH.O$, a true aldehyde alcohol, is a tri-derivative of butane.

In order to prepare it, a mixture of ethylic aldehyde with dilute hydrochloric acid, after standing fourteen days, is neutralised with soda and shaken with ether. The ethereal layer is removed, and yields on evaporation impure aldol, from which, by distillation under reduced pressure (at 2 c.m. pressure between 95° and 105°), pure aldol is obtained. It is a mobile liquid miscible with water, sp. gr. 1·1208 at 0°. Its formation occurs according to the equation :



$$\begin{array}{l}CH_3\\ |\\ CH : O\\ \\ CH_3\\ |\\ CH : O\end{array} = \begin{array}{l}CH_3\\ |\\ CH.OH\\ |\\ CH_2\\ |\\ CH : O\end{array}$$

After some time it changes into a viscous transparent mass, probably a polymeric modification, and is then no longer soluble in water. This loses water on gentle heating in a stream of air, and crystals slowly separate of the formula $C_8H_{14}O_3$:



$$2CH_3.CH(OH).CH_2.CH:O = H_2O + \begin{array}{c} CH_3.CH.CH_2.CH:O \\ | \\ O \\ | \\ CH_3.CH.CH_2.CH:O \end{array}$$

which stands in the same relation to aldol as ether to alcohol. The crystals melt at 155° and distil under reduced pressure at 157°.

Aldol reduces argentic oxide and is converted into β-oxybutyric acid:

$$CH_3.CH(OH).CH_2.CHO + Ag_2O$$
$$= Ag_2 + CH_3.CH(OH).CH_2.CO.OH.$$

On distillation under ordinary atmospheric pressure water is eliminated and crotonic aldehyde formed:

$$CH_3.CH(OH).CH_2.CHO = H_2O + CH_3.CH:CH.CHO.$$

Ammonia unites directly with aldol, as with the ordinary aldehydes:

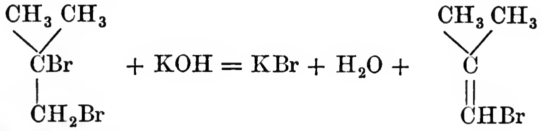
$$CH_3.CH(OH).CH_2.CHO + NH_3$$
$$= CH_3.CH(OH).CH_2.CH(OH)NH_2.$$

Aldol ammonia is a solid mass which dissolves in water and smells like the aldehyde ammonias.

Nascent hydrogen converts aldol into β-butylene glycol (§ 489, 1):

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

657. *Isobutenyl Compounds.*—If isobutylene dibromide be heated with alcoholic potassic hydrate, *isocrotyl bromide* is formed:



as a colourless oily liquid of sharp odour, boiling at 91°; on heating with sodic ethylate to 150°–170° in sealed tubes it is converted into *isocrotyl ethyl ether*:

$$(CH_3)_2:C:CHBr + NaOC_2H_5$$
$$= NaBr + (CH_3)_2:C:CH.O:OC_2H_5.$$

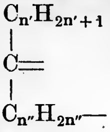
This latter is an oil, lighter than water, and boiling at 92°–94°; it unites with bromine to form

Isobutenyl dibromide ethylate, $(CH_3)_2:CBr.CHBr.O.C_2H_5$, and is oxidised by chromic acid into acetone, carbonic anhydride, and acetic acid:

$$(CH_3)_2:C:CH.OC_2H_5 + 5O = (CH_3)_2CO + CO_2$$
$$+ HO.CO.CH_3 + H_2O.$$

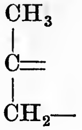
DERIVATIVES OF THE KETONE ALCOHOL RADICALS, C_nH_{2n-1}.

658. The group of ketone alcohol radicals:



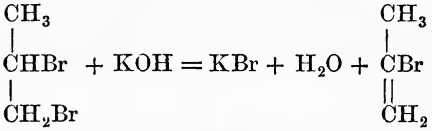
$$\begin{array}{l} C_{n'}H_{2n'+1} \\ | \\ C= \\ | \\ C_{n''}H_{2n''}- \end{array}$$

is chiefly represented by derivatives of acetone and propylene, i.e. of the hydro-carbon nucleus:



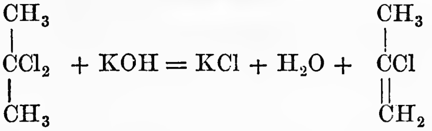
$$\begin{array}{l} CH_3 \\ | \\ C= \\ | \\ CH_2- \end{array}$$

The unsaturated bodies of this class are the monosubstituted propylenes, which are obtained by the action of alcoholic potassic hydrate upon propylene dihaloids (§ 478):



$$\begin{array}{lcl} CH_3 & & CH_3 \\ | & & | \\ CHBr & + KOH = KBr + H_2O + & CBr \\ | & & \| \\ CH_2Br & & CH_2 \end{array}$$

and on the dihaloids of the acetone radical (§ 445):



$$\begin{array}{lcl} CH_3 & & CH_3 \\ | & & | \\ CCl_2 & + KOH = KCl + H_2O + & CCl \\ | & & \| \\ CH_3 & & CH_2 \end{array}$$

Monochlor propylene, $CH_3.CCl:CH_2$, boils at 23°, and below that temperature forms a liquid little soluble in water.

Monobrom propylene, $CH_3.CBr:CH_2$, boils at 57°–58°.

659. By the union of these two compounds with halogens the trihaloids of the radicals are obtained as liquids insoluble in water.

Chlor-propylene dichloride, $CH_3.CCl_2.CH_2Cl$, boils at 123°; it is also obtained by the action of phosphoric chloride on monochlor acetone:

$$CH_3.CO.CH_2Cl + PCl_5 = CH_3.CCl_2.CH_2Cl + POCl_3,$$

and by the action of chlorine on methyl chlor-acetol (§ 445) in sunlight:

$$CH_3.CCl_2.CH_3 + Cl_2 = HCl + CH_3.CCl_2.CH_2Cl + HCl.$$

It is isomeric with propenyl trichloride (§ 665).

Brom-propylene dibromide, $CH_3.CBr_2.CH_2Br$, is an oil of powerful burning odour, of sp. gr. 3·392 at 23°, and boiling at 195°. The same compound is obtained when the vapours of propylene dibromide and bromine are brought together.

Chlor-propylene dibromide, $CH_3.CClBr.CH_2Br$, prepared from monochlor propylene and bromine, boils at about 170°, and has sp. gr. 2·064 at 0°.

660. *Monosubstitution Products of Acetone.—Monochlor acetone,* $CH_3.CO.CH_2Cl$, is obtained by oxidation of monochlor propylene by an aqueous solution of hypochlorous acid:

$$CH_3.CCl:CH_2 + HOCl = HCl + CH_3.CO.CH_2Cl,$$

by oxidation of propylene hydrate chloride (§ 496), and by the action of chlorine on acetone. In the latter case well-cooled acetone is saturated with chlorine and the monochlor acetone separated by fractional distillation. It is a colourless liquid which attacks the mucous membrane and tear glands, is insoluble in water, boils at 119°, and has sp. gr. 1·17.

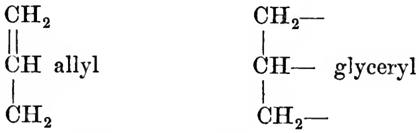
Acetate of acetonalcohol, $CH_3.CO.CH_2.O.C_2H_3O$, is obtained by heating monochlor acetone for some time with an alcoholic solution of potassic acetate, as a liquid of refreshing odour, boiling at about 175°, and having sp. gr. 1·053 at 11°. It is soluble in water, but soon decomposes therewith.

661. *Monobrom butylene,* $CH_3.CH_2.CBr.CH_2$, is formed from butylene dibromide by action of alcoholic potassic hydrate as a colourless oil, boiling at 140°–150°, and uniting with two atoms of bromine to form

Butenyl tribromide, $CH_3.CH_2.CBr_2.CH_2Br$, a liquid not miscible with water, boiling with decomposition at 208°–215°.

DERIVATIVES OF THE TRIVALENT ALCOHOL RADICALS, C_nH_{2n-1}.

662. Nearly the only compounds of trivalent alcohol radicals known are the derivatives of the tricarbon radical C_3H_5. This, when rendered monovalent by the double union of two of its carbon atoms, forms the radical *allyl,* and when in the trivalent state the radical *glyceryl:*



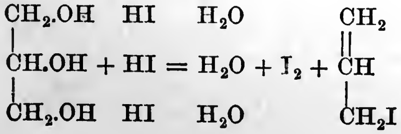
$$\begin{array}{lll} CH_2 & & CH_2- \\ \| & & | \\ CH & \text{allyl} \qquad & CH- \quad \text{glyceryl} \\ | & & | \\ CH_2 & & CH_2- \end{array}$$

Allyl Compounds.

663. *Diallyl sulphide* and *allyl mustard oil* are found in nature, the former in leeks and onions, the latter as product of the fermentation of the myronic acid contained in black mustard seeds.

Allyl compounds can all be obtained artificially from the trivalent alcohol glycerine.

By treating glycerine 15 parts with 10 parts iodine and 6 of amorphous phosphorus, and heating, allyl iodide is obtained and may be separated from the isopropyl iodide formed at the same time by distillation (§ 192):



$$\begin{array}{llllll} CH_2.OH & HI & H_2O & & & CH_2 \\ | & & & & & \| \\ CH.OH & + HI = & H_2O & + I_2 & + & CH \\ | & & & & & | \\ CH_2.OH & HI & H_2O & & & CH_2I \end{array}$$

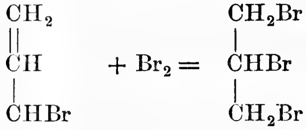
The allyl iodide can then, similarly to the alkyl iodides, be converted into the salts of allyl, and these again by saponification into allyl alcohol.

By slowly heating a mixture of 4 parts glycerine with 1 of crystallised oxalic acid, with addition of a little ammonic chloride, to between 220° and 230°, and then to about 260°, a mixture first passes over of aqueous formic acid and allyl alcohol, and above 195° glycerine monoformate principally distils, which by repeated distillation splits up into water, carbonic oxide, and allyl alcohol:

$$C_3H_5(OH)_2O.CHO = CO_2 + OH_2 + C_3H_5.OH.$$

After saturating the collected distillates with K_2CO_3 the allyl alcohol separates on the surface, and is further purified by distillation first over solid KHO and finally over BaO.

The general behaviour of the allyl compounds is quite analogous to that of the alkyl derivatives. The most important difference consists in that the allyl compounds, as primary substitution products of propylene, enter into direct combination with the halogens and hypochlorous acid, &c., to form glycerine compounds:



$$\begin{array}{ccc} CH_2 & & CH_2Br \\ \| & & | \\ CH & + Br_2 = & CHBr \\ | & & | \\ CHBr & & CH_2Br \end{array}$$

Allyl bromide, or γ-brom-propylene. Glycerine tribromide.

664. *Halogen Compounds of Allyl.—Allyl chloride:*

$$CH_2:CH.CH_2Cl,$$

isomeric with monochlor propylene (§ 658), is prepared by the action of PCl_3 or HCl on allyl alcohol:

$$CH_2:CH.CH_2.OH + HCl = CH_2:CH.CH_2.Cl + OH_2,$$

and also from allyl iodide by the action of $HgCl_2$:

$$2C_3H_5I + HgCl_2 = 2C_3H_5Cl + HgI_2.$$

It is a colourless liquid, of disagreeable smell, boiling at 46°, insoluble in water, and having at 0° the sp. gr. ·954.

Allyl bromide, C_3H_5Br, resembles the chloride; it boils between 70°–71°; sp. gr. 1·461 at 0°. It combines with HBr to trimethene dibromide (§ 479).

Allyl iodide, $CH_2:CH.CH_2I$, is an oily liquid of sp. gr. 1·789 at 16°, smells strongly like leeks, and boils at 101°. It is converted by zinc and HCl into propylene (§ 658), by heating with HI into propylene and isopropyl iodide:

$$CH_2:CH.CH_2I + HI = I_2 + CH_2:CH.CH_3$$
$$CH_2:CH.CH_2I + 2HI = I_2 + CH_2.CHI.CH_3.$$

On agitating an alcoholic solution of C_3H_5I with metallic mercury, colourless, leafy crystals, quickly turning yellow in sunlight, of mercury allyl iodide (comp. § 361) crystallise out:

$$CH_2:CH.CH_2I + Hg = CH_2:CH.CH_2.HgI,$$

which, treated with HI, yield propylene gas :

$$CH_2{:}CH.CH_2.HgI + HI = CH_2{:}CH.CH_3 + HgI_2.$$

665. *Allyl alcohol,* $CH_2{:}CH.CH_2.OH$, obtained as above described, is a colourless and mobile liquid of a sharp smell and sp. gr. at 0° of ·858. It boils between 96° and 97°, and crystallises to a colourless mass at a temperature of −50°. It combines directly with the halogens to glycerine monohydro-dihaloids, e.g.

$$CH_2Cl.CHCl.CH_2.OH.$$

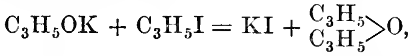
By oxidising agents it is converted first into acroleïn and then into formic acid.

Nascent hydrogen does not combine with it at the ordinary temperature, but by heating with potash to 100°–105° formic acid, ethyl alcohol, primary propyl alcohol, and some products containing less hydrogen, which have not been much investigated, are produced. Potassium and sodium dissolve in allyl alcohol with disengagement of hydrogen and formation of bodies analogous to the alkylates of the alkalies :

$$2CH_2{:}CH.CH_2.OH + Na_2 = H_2 + 2CH_2{:}CH.CH_2.ONa.$$

666. *Ether-like compounds* of allyl are obtained by the reaction between metallic allylates and the halogen compounds of the alcohol radical.

Allyl ether, or *diallyl oxide,* $(CH_2{:}CH.CH_2)_2O$, is formed according to the following equation :



$$C_3H_5OK + C_3H_5I = KI + \begin{matrix}C_3H_5\\C_3H_5\end{matrix}\!\!>O,$$

and also by the action of allyl iodide on the oxides of mercury or silver :

$$2C_3H_5I + Ag_2O = (C_3H_5)_2O + 2AgI.$$

It is a colourless liquid, insoluble in water, boiling at 82°. A small quantity appears to occur naturally in oil of garlic.

Allyl-methyl ether, $CH_2{:}CH.CH_2.O.CH_3$, from sodic methylate and allyl iodide, is a colourless liquid boiling at 46°.

Allyl-ethyl ether, $CH_2{:}CH.CH_2.O.CH_2.CH_3$, obtained in a similar manner, boils at 64°.

667. *The allyl salts* are most easily obtained by the reaction between allyl iodide and the silver salts of the acids.

Allyl acetate, $CH_2{:}CH.CH_2.O.CO.CH_3$, boils between 98° and 100°. The *formate* is found in small quantities, along with formic acid and allyl alcohol, among the products resulting from heating glycerine with oxalic acid. It is lighter than water and boils between 82° and 83°. Both salts have a very sharp smell.

Allyl butyrate boils at 140°, *isovalerate* about 162°.

Monallyl sulphate, $C_3H_5.HSO_4$, is formed by mixing H_2SO_4 and allyl alcohol; its barium salt is soluble in water.

Allyl nitrate, $CH_2{:}CH.CH_2.O.NO_2$, boils at 106°, sp. gr. 1·09 at 10°.

668. *Allyl Sulphur Compounds.—Thio-allyl alcohol,* or *allyl mer-*

captan, $CH_2:CH.CH_2.SH$, is formed by the action of C_3H_5I on an alcoholic solution of potassic sulph-hydrate:

$$C_3H_5I + KSH = KI + C_3H_5.SH.$$

It is very similar to the ethyl mercaptan, and boils at 90°. The sulphur is easily replaced by metals, especially mercury.

It gives by oxidation with nitric acid *allyl sulphonic acid*, $CH_2:CH.CH_2.SO_2.OH$, the barium salt of which crystallises in shining prisms.

Diallyl sulphide, or *thio-allyl ether*:

$$CH_2:CH.CH_2.S.CH_2.CH:CH_2,$$

is the principal constituent of the yellow ethereal oil obtained by distilling garlic (*Allium sativum*) with water, from which it is obtained by repeated fractionation and rectification over potassium. It also occurs in the leaves and seeds of many Cruciferæ (*Alliaria officinalis*, &c.), and is obtained synthetically by the reaction between C_3H_5I and K_2S in alcoholic solution.

In the pure form it is a colourless oil, of a powerful garlic-like odour, boiling at 140°.

669. *Nitrogen Compounds of Allyl.*—Allyl yields with nitrogen compounds similar to those of the alcohol radicals.

Allyl iodide and ammonia react, forming the iodides of the various allylamines, from which a mixture of the free bases is liberated by treatment with potassic hydrate. The separation of the individual constituents in a state of purity is attended with the usual difficulties.

Allylamine, $CH_2:CH.CH_2.NH_2$, is most easily obtained in the pure form by reducing allyl mustard oil with zinc and HCl in alcoholic solution:

$$CH_2:CH.CH_2.N:CS + 2Zn + 5HCl = CH_2:CH.CH_2.NH_2HCl \\ + 2ZnCl_2 + CH_2S.$$

On distilling the product of the reaction with OKH, it is obtained as an ammoniacal liquid of sp. gr. ·864 and boiling point 58°.

The principal product of the reaction between allyl iodide and ammonia:

$$4C_3H_5I + 4NH_3 = 3NH_4I + N(C_3H_5)_3I,$$

tetrallyl ammonium iodide, is precipitated from its aqueous solution by KHO as a syrup, and crystallises in vacuo over H_2SO_4 after some time. By treating its solution with argentic hydrate *tetrallyl ammonium hydrate*, $N(C_3H_5)_4OH$, a caustic alkaline liquid, is obtained, which on heating decomposes principally into *triallylamine*, $N(C_3H_5)_3$, a basic volatile oil.

670. *Allyl pseudo-cyanate*, or *allyl carboxylamine*:

$$CH_2:CH.CH_2.N:CO,$$

is formed by heating allyl iodide and potassic pseudo-cyanate together. It is a sharp-smelling oil, which boils at 82° and excites to tears. By gently heating with water it splits up into CO_2 and *diallyl urea*, or *sinapoline* (comp. § 280):

$$2C_3H_5.N:CO + OH_2 = CO_2 + (C_3H_5)HN.CO.NH(C_3H_5),$$

which crystallises in large leafy crystals, melting at 100°.

It combines directly with ammonia to form *monallyl urea:*

$$C_3H_5.N:CO + NH_3 = (C_3H_5).HN.CO.NH_2,$$

and with ethylamine to form *ethyl-allyl urea:*

$$(C_3H_5).HN.CO.NH(C_2H_5),$$

which crystallises in fine prisms.

671. *Allyl mustard oil,* or *allyl pseudo-sulpho-cyanate:*

$$CH_2:CH.CH_2.N:C:S$$

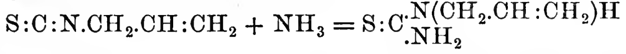
(comp. §§ 284 and 285). Black mustard seeds contain the potassium salt of a glucoside acid, *myronic acid*, which, in presence of water and a ferment existing in the seeds (*myrosine*), is converted into sugar, hydric potassic sulphate, and allyl mustard oil. The very powerful odour of mustard oil is indeed evident after slightly moistening the seeds with water. The oil is obtained by distillation with water, and purified by further fractional distillation. It possesses the sp. gr. 1·017 at 10°, and boils between 150° and 151°; its vapour density is 3·4. It is insoluble in water, but mixes freely with alcohol and ether.

The liquid raises blisters on the skin, and its vapour powerfully irritates the mucous membranes.

Synthetically it may be obtained by the reaction between C_3H_5I and potassium sulpho-cyanate in alcoholic solutions (difference from the alkyl mustard oils).

Ammonia forms with mustard oil

Allyl thio-urea, or *thio-sinnamine:*



$$S:C:N.CH_2.CH:CH_2 + NH_3 = S:C\begin{matrix}N(CH_2.CH:CH_2)H \\ .NH_2\end{matrix}$$

which crystallises in colourless rhombic prisms, of bitter taste, melting at 74°, and soluble in water, alcohol, and ether. It combines with monobasic acids to acid, easily decomposable salts, and also gives compounds with metallic salts like mercuric chloride and silver nitrate.

Allyl pseudo-sulpho-cyanate combines with ethylamine to form *allyl-ethyl thio-urea,* $(C_3H_5)HN.CS.NH.C_2H_5$, a difficultly crystallisable syrup.

672. By heating an aqueous solution of sulph-allyl urea with plumbic oxide the sulphur is removed and allyl cyanamide formed (see § 276).

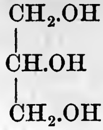
Allyl cyanamide is obtained as a syrupy mass after separating the lead from the solution by SH_2 and evaporating. It gradually changes or metamerises into *triallyl melamine* or *sinnamine*, $C_3N_6(C_3H_5)_3H_3$, which is soluble in water, alcohol, and ether, has a bitter taste, and reacts alkaline.

Allyl nitryl, $CH_2:CH.CH_2.NO_2$, formed by the double decomposition between allyl iodide and argentic nitrite, is an oil heavier than water which boils at 96°.

Compounds of Glycerine.

673. The glycerine derivatives contain the same radical as the allyl compounds, but with single combination between the carbon atoms, so that it acts towards other radicals or elements as a trivalent group.

Either the triatomic alcohol glycerine or the compounds of allyl serve as raw material from which the glycerine compounds may be formed.



$$\textit{Glycerine},\ C_3H_5(OH)_3 = \begin{array}{l} CH_2.OH \\ | \\ CH.OH \\ | \\ CH_2.OH \end{array}$$

674. The naturally occurring fats, both from plants and animals, are the neutral salts of the triatomic alcohol glycerine with the $C_nH_{2n-1}O.OH$ and the $C_nH_{2n-3}O.OH$ series of acids and a few others. As previously explained (§ 561), the fats are decomposed by boiling with strongly basic hydrates into the salts of the particular acids and glycerine (saponification).

If the alkalies are used as saponifying agents the glycerine can be obtained pure only with difficulty :

$$C_3H_5(OC_nH_{2n-1}O)_3 + 3KHO = 3KO.C_nH_{2n-1}O + C_3H_5(OH)_3.$$

In this case the mixture of soap and glycerine is neutralised with the proper amount of H_2SO_4, the fatty acid which separates removed mechanically, and the aqueous solution evaporated as far as possible. The residue is a mixture of alkaline sulphate and glycerine ; the latter is removed by absolute alcohol, from which it is again obtained as a syrup on distilling off the alcohol. The saponification is much more conveniently made with plumbic oxide and water, whereby an insoluble lead salt is formed, from which the glycerine solution is filtered and a little dissolved lead removed by means of SH_2. On the manufacturing scale glycerine is obtained by distillation of fats with superheated steam, producing insoluble fatty acid and pure glycerine. Glycerine can be obtained in several ways from allyl compounds, most conveniently by combining allyl bromide with bromine to form the tribromide, converting this by heating with silver acetate into glyceryl triacetate, which can be easily saponified into acetic salts and glycerine :

$$C_3H_5Br_3 + 3AgOC_2H_3O = 3AgBr + C_3H_5(OC_2H_3O)_3.$$

From propylene, and therefore from acetone and isopropyl alcohol, glycerine can be obtained by means of propylene dichloride.

The latter is converted, by heating with iodine chloride to 140°, into glycerine trichloride (§ 655), which further, by heating with much water to 170°, is converted into glycerine :

$$C_3H_5Cl_3 + 3HOH + xOH_2 = C_3H_5(OH)_3 + 3HCl + xOH_2.$$

Small quantities of glycerine are also formed during the alcoholic fermentation of sugar. Consequently it is found in small quantities in such alcoholic beverages as are not distilled.

675. Glycerine in the ordinary condition is a syrupy liquid of very sweet taste ; it can, however, by means of cold and simultaneous shaking, be obtained in fine crystalline masses.

It is soluble in water and alcohol, but scarcely in ether. By heating in open vessels to 170° it is rendered anhydrous, and then possesses the sp. gr. 1·27. It absorbs moisture from the atmosphere. Under ordinary pressure glycerine boils at 280°, with partial decomposition; in a vacuum of 50 mm. the boiling point is 210°, at 12 mm. 179·5°. It is easily carried over with steam.

When distilled with dehydrating substances, such as P_2O_5 or potassic hydric sulphate, acroleïn is formed:

$$C_3H_5(OH)_3 = 2OH_2 + C_3H_4O;$$

with melted potash, acetate, formate, and free hydrogen are yielded:

$$C_3H_5(OH)_3 + 2KOH = KO.CHO + KO.C_2H_3O + OH_2 + 2H_2.$$

Phosphorus iodide and HI convert it, according to the proportion used, into allyl iodide, propylene, or isopropyl iodide (§ 192).

A weak aqueous solution of glycerine is slowly fermented by contact with yeast at 20° to 30°, propionic acid being formed:

$$CH_2(OH).CH(OH).CH_2.OH = CH_3.CH_2.CO.OH + OH_2.$$

676. *Metallic Compounds.*—Glycerine dissolves metallic oxides in certain proportions, and not alone the alkali metals, but also calcium, barium, lead, and copper oxides, undoubtedly forming metallic derivatives of glycerine. The copper compound may be

$$C_3H_5(OH)_2.O.Cu.O.C_3H_5(OH)_2\ (?),$$

from whose solutions alkalies do not precipitate the copper.

Many salts are also very largely dissolved by glycerine—e.g. sodic chloride, and also arsenious anhydride.

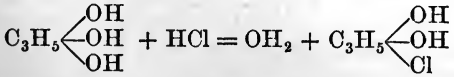
Sodium does not act on dry glycerine at ordinary temperatures; on warming, however, the reaction is so violent that the sodium becomes nearly red hot, and the glycerine is carbonised with production of acroleïn. On warming with sodium amalgam the reaction takes place quietly, a crystalline compound being obtained after the addition of alcohol of the form $C_3H_5(ONa)(OH)_2.C_2H_5OH$. The same body is, however, much more easily formed by adding glycerine to a solution of sodium ethylate in absolute alcohol. The sodium compound crystallises out almost immediately, and may be freed from the alcohol molecule by heating to 100° in a stream of hydrogen.

Sodic glycerate is a white, very hygroscopic substance, easily decomposed by water into glycerine and sodic hydrate.

Haloid Derivatives of Glycerine.

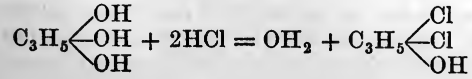
677. The three hydroxyl groups in glycerine can be individually replaced by halogens.

By treatment of glycerine with the halogen acids, one or two of the hydroxyls can be replaced according to the relative proportions operated upon—temperature, presence of water, &c. The mono- and dihaloid compounds are generally simultaneously formed, but the reaction can never be carried out quantitatively:



$$C_3H_5\left\langle\begin{matrix}OH\\OH\\OH\end{matrix}\right. + HCl = OH_2 + C_3H_5\left\langle\begin{matrix}OH\\OH\\Cl\end{matrix}\right.$$

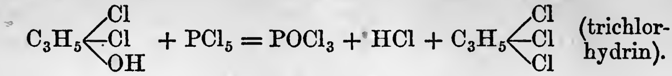
(monochlorhydrin).



$$C_3H_5\left\langle\begin{matrix}OH\\OH\\OH\end{matrix}\right. + 2HCl = OH_2 + C_3H_5\left\langle\begin{matrix}Cl\\Cl\\OH\end{matrix}\right.$$

(dichlorhydrin).

To remove the last OH group recourse must be had to the pentahaloid phosphorus compounds :



$$C_3H_5\left<\begin{matrix}Cl\\Cl\\OH\end{matrix}\right. + PCl_5 = POCl_3 + HCl + C_3H_5\left<\begin{matrix}Cl\\Cl\\Cl\end{matrix}\right. \text{(trichlorhydrin).}$$

Haloid glycerines can be formed from the allyl series by addition of halogens, hypochlorous acid, and haloid acids, as described in another place.

By heating the glycerine haloids or haloid hydrates with metallic acetates the halogen atoms are replaced by $O.C_2H_3O$, yielding glycerine acetates, from which, on saponification, glycerine is obtained.

678. *Monochlorhydrin*, $C_3H_5.(OH)_2Cl$, doubtless exists in two isomeric forms, namely :

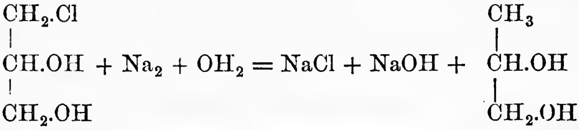
$$\begin{matrix}CH_2.Cl\\|\\CH.OH\\|\\CH_2.OH\end{matrix} \quad \text{and} \quad \begin{matrix}CH_2.OH\\|\\CH.Cl\\|\\CH_2.OH\end{matrix}$$

which, however, are not yet known in the pure state. It is very probable that a mixture of the two bodies is formed when glycerine saturated with HCl is heated for a long time at 100°, and afterwards fractionally distilled.

Allyl alcohol combines with hypochlorous acid with evolution of heat, and the chlorhydrin is left, after evaporating the liquid on the water bath, as a thick sweet and sharp-tasting liquid, of sp. gr. 1·4 at 13° and boiling between 230° and 235°.

From its high boiling point it is probably the double primary hydrate $CH_2(OH).CHCl.CH_2(OH)$.

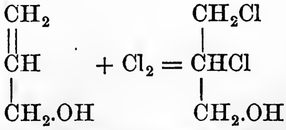
The preparation from glycerine certainly contains the primary-secondary hydrate in greater proportion, since its aqueous solution is reduced by sodium amalgam principally to propylene glycol (§ 488) :



$$\begin{matrix}CH_2.Cl\\|\\CH.OH\\|\\CH_2.OH\end{matrix} + Na_2 + OH_2 = NaCl + NaOH + \begin{matrix}CH_3\\|\\CH.OH\\|\\CH_2.OH\end{matrix}$$

679. *Dichlorhydrin*, $C_3H_5.Cl_2.OH$, is known in both its isomeric forms.

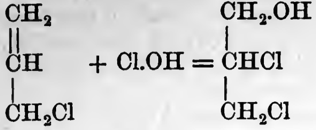
a. The *primary* hydrate is obtained pure by passing chlorine into anhydrous allyl alcohol cooled by ice :



$$\begin{matrix}CH_2\\||\\CH\\|\\CH_2.OH\end{matrix} + Cl_2 = \begin{matrix}CH_2Cl\\|\\CHCl\\|\\CH_2.OH\end{matrix}$$

as a mobile, colourless liquid, soluble in much water, of sp. gr. 1·3799 at 0° and 182° boiling point.

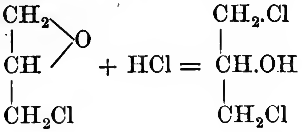
On account of its method of formation it is called *allyl-alcohol dichloride*, and can also be considered as *dichlor-propyl alcohol*. The same compound is formed directly from allyl chloride and hypochlorous acid:



$$\begin{array}{l} \mathrm{CH_2} \\ \| \\ \mathrm{CH} \\ | \\ \mathrm{CH_2Cl} \end{array} + \mathrm{Cl.OH} = \begin{array}{l} \mathrm{CH_2.OH} \\ | \\ \mathrm{CHCl} \\ | \\ \mathrm{CH_2Cl} \end{array}$$

Sodium takes away the two chlorine atoms, reforming allyl alcohol, which by excess of sodium passes into the allylate.

β. The *secondary* hydrate, $CH_2Cl,CH(OH),CH_2Cl$, commonly and improperly called *dichlorhydrin*, properly *dichlor-isopropyl alcohol*, is obtained in the pure state by mixing *epichlorhydrin* with HCl. The combination takes place with evolution of heat:



$$\begin{array}{l} \mathrm{CH_2} \diagdown \\ | \quad\;\; \rangle \mathrm{O} \\ \mathrm{CH} \diagup \\ | \\ \mathrm{CH_2Cl} \end{array} + \mathrm{HCl} = \begin{array}{l} \mathrm{CH_2.Cl} \\ | \\ \mathrm{CH.OH} \\ | \\ \mathrm{CH_2Cl} \end{array}$$

The β-dichlorhydrin is a mobile liquid of agreeable smell, boiling at 174°, therefore 8° lower than α, and of sp. gr. 1·383 at 19°. It mixes with alcohol and ether, and dissolves in nine times its volume of water.

Sodium amalgam converts it into isopropyl alcohol:

$$CH_2Cl.CH(OH).CH_2Cl + 2Na_2 + 2OH_2 = 2NaCl + 2NaOH \\ + CH_3.CH(OH).CH_3.$$

It yields, by oxidation with dilute chromic and sulphuric acids, a dichlor acetone of the form $CH_2Cl.CO.CH_2Cl$.

The two isomers are formed together by long-continued heating of one volume of glycerine and twelve volumes of fuming HCl to 100°, and fractionation of the product; more conveniently by saturating a mixture of glacial acetic acid and glycerine with HCl at 100°. The dichlorhydrin, boiling at 174°, generally predominates; and when the temperature at which the mixture is saturated with HCl exceeds 100° it is the sole product. By this last method some acetate chloride is also formed.

An excellent yield of dichlorhydrin is obtained by gradually adding one molecule of glycerine to two of sulphur chloride, with continuous shaking and warming on the water bath, until the sulphur has separated in a compact state. It may then be purified by distillation:

$$C_3H_5(OH)_3 + 2S_2Cl_2 = 2HCl + SO_2 + 3S + C_3H_5(OH)Cl_2.$$

Both the α- and β-chlorhydrins are converted by concentrated alkalies into *epichlorhydrin*.

680. *Trichlorhydrin*, or *glyceryl trichloride*, $CH_2Cl.CHCl.CH_2Cl$, isomeric with propylene trichloride (§ 655) and chlor-propylene dichloride (§ 659), is obtained by the action of PCl_5 on the two previous compounds. It is separated from the simultaneously formed $POCl_3$ by washing with water and distillation.

It is a colourless, mobile liquid, with an odour similar to that of chloroform, boiling at 158° and of sp. gr. 1·417 at 15°.

Trichlorhydrin is also produced by the direct addition of chlorine to allyl chloride, $CH_2 : CH.CH_2Cl + Cl_2 = CH_2Cl.CHCl.CH_2Cl$, and, along with the isomeric propylene trichloride, by heating propylene dichloride with iodine chloride.

Solid caustic alkalies convert it into *dichlor glycid* :

$$C_3H_5Cl_3 + KOH = KCl + H_2O + C_3H_4Cl_2.$$

681. The *bromides* of glycerine correspond in properties and methods of formation to the chlorides, differing mostly from the latter by their greater density and higher boiling point.

Monobromhydrin, $C_3H_5(OH)_2Br$, is a thick liquid only distilling unchanged in vacuo at 180°.

Glyceryl dibrom-hydrate. Both isomers are known.

α-Allyl-alcohol dibromide, or *dibrom-propyl alcohol :*

$$CH_2Br.CHBr.CH_2OH,$$

prepared by the direct combination of bromine and allyl alcohol, boils between 212° and 214°.

β-Dibromhydrin, dibrom-isopropyl alcohol :

$$CH_2Br.CH(OH)CH_2Br,$$

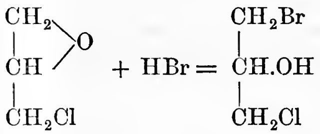
from glycerine and HBr, boils at 219° and has the sp. gr. 2·11 at 18°.

Tribromhydrin, $CH_2Br.CHBr.CH_2Br$, isomeric with brom-propylene dibromide, is obtained from the previous compounds by means of phosphorus bromide, and also from allyl bromide or iodide and bromine :

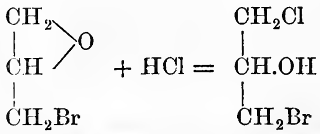
$$CH_2 : CH.CH_2I + 2Br_2 = CH_2Br.CHBr.CH_2Br + IBr.$$

It crystallises in colourless shining prisms, melting at 16° and boiling between 219° and 220°.

682. *Chlor-brom-hydrin*, $C_3H_5.Cl.Br.OH$, is formed by the action of hydrobromic acid on epichlorhydrin :



or by action of hydrochloric acid on epibromhydrin :



It is an oily body, boiling at 197°, of sp. gr. 1·740 at 12°.

The *chlor-allyl dibromide*, of the formula $CH_2Br.CHBr.CH_2Cl$, may be regarded as *glyceryl chloride-dibromide* ; it boils at 195° and has the sp. gr. 2·088.

The isomeric *chlor-dibrom-hydrin*, $CH_2Br.CHCl.CH_2Br$, which boils between 202° and 203°, is a product of the action of PCl_5 on dibromhydrin.

Both compounds are isomeric with chlor-propylene dibromide.

Brom-dichlor-hydrin is obtained quite in an analogous manner from dichlorhydrin and PBr_5. It boils at 176° and has the formula $CH_2Cl.CHBr.CH_2Cl$.

683. A *moniodo-hydrin*, $C_3H_5I(OH)_2$, is obtained by heating glycerine saturated with HI to 100° for forty hours, and after neutralising the free acid with alkali shaking out with ether. The latter leaves on evaporation iod-hydrine, a yellow syrup slightly soluble in water, of sp. gr. 1·783, which decomposes on distillation.

Diiodo-hydrin, $CH_2I.CH(OH).CH_2I$. The product of long-continued heating of dichlorhydrin with a concentrated solution of potassic iodide is a thick oil of sp. gr. 2·4. It crystallises at $-16°$ to colourless crystals, and decomposes on heating with formation of allyl alcohol, allyl iodide, and acroleïn, and evolution of iodine.

Chlor-iodhydrin, $CH_2Cl.CH(OH)CH_2I$, prepared by direct combination of epichlorhydrin and HI, boils at 226° under partial decomposition; sp. gr. 2·06 at 10°.

The corresponding bromine compound, $(CH_2Br.CH(OH).CH_2I)$, is not capable of being distilled.

Triiodo-hydrin, or *glycerine triiodide*, is not capable of existing, decomposing at once into iodine and allyl iodide. Several trihaloid glycerine compounds are known, however—viz. iodhydrin and PCl_5 give $CH_2Cl.CHCl.CH_2I$, boiling at 205°, sp. gr. 2·0476 at 9°; and $CH_2Cl.CHBr.CH_2Cl$, from chloriod-hydrins and PBr_5, decomposed by distillation, sp. gr. 2·325 at 9°.

Ethereal Derivatives of Glycerine.

684. These bodies are easily obtained by the reaction between haloid glycerine and the sodium alcoholates (e.g. sodic ethylate).

Monochlorhydrin yields in this manner with sodium ethylate *ethyl hydrin*, or *ethylin*, a liquid boiling at 230° and soluble in water:

$$C_3H_5(OH)_2Cl + NaO.C_2H_5 = NaCl + C_3H_5(OH)_2(O.C_2H_5);$$

dichlorhydrin yielding a *diethylin*, $CH_2(OC_2H_5)CHOH.CH_2.OC_2H_5$, boiling at 182°–183°, possessing a faint odour of pepper, sp. gr. ·92.

This compound dissolves sodium and reacts again with ethyl iodide, forming *triethylin*:

$$C_3H_5(O.C_2H_5)_2.ONa + C_2H_5I = NaI + C_3H_5(O.C_2H_5)_3.$$

It is insoluble in water and boils at 185°.

685. A *glycerine chloride hydrate ethylate*, or *ethyl chlor-hydrin*, is formed when (§ 666) allyl-ethyl ether comes in contact with diluted hypochlorous acid:

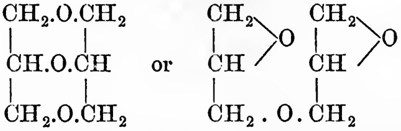
$$CH_2:CH.CH_2.O.C_2H_5 + ClOH = CH_2(OH).CHCl.CH_2.O.C_2H_5.$$

It may be extracted from its aqueous solution by ether, and remains on evaporation of that solvent as a thick liquid of faintly ethereal odour, boiling between 183° and 185°, of sp. gr. 1·117 at 11°.

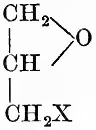
By the combination of cooled allyl-ethyl ether with chlorine, a *glycerine dichlorethylate*, $CH_2Cl.CHCl.CH_2.O.C_2H_5$, boiling at 165°, is formed. The corresponding bromine compound also exists, boiling at 195°. Metallic sodium extracts the halogen from both bodies, reforming the allyl-ethyl ether.

Allylin, $C_3H_5(OH)_2O.CH_2.CH:CH_2$, or glyceryl dihydrate allyl ether, can be isolated from the following compound by fractional distillation of the residue remaining in the retorts after the preparation of allyl alcohol from glycerine by heating with oxalic acid. It is a thick liquid boiling between 225° and 240°, and combines directly with bromine to form $C_3H_5(OH)_2.O.C_3H_5Br_2$.

Glyceryl ether, $(C_3H_5)_2O_3$, obtained along with the above, is a colourless, odourless liquid, soluble in water, and boiling between 169° and 172°. It has not yet been determined which of the two following formulæ represents its constitution :

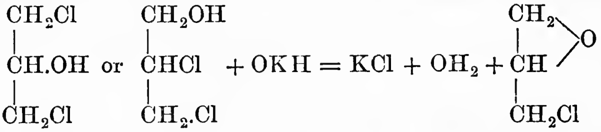


686. To the ethereal derivatives belong also the *glyceryl oxyhaloid* compounds, or *epihaloid hydrins*, and other bodies constituted on the general formula :

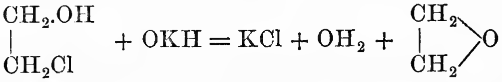


(for analogous bodies see § 499).

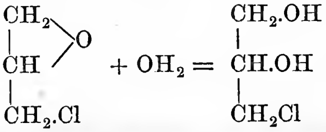
They are formed by the action of alkalies on glyceryl dihaloid hydrates ; e.g.



corresponding to :



They combine directly with water to form glyceryl dihydrate haloids, the haloid having a primary position :

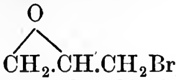


and with the haloid acids to the above-described dihaloid hydrins.

Epichlorhydrin, or *glyceryl oxychloride :*

isomeric with monochlor acetone (§ 660), is easily formed from the glyceryl dichlorides. Dichlorhydrin, boiling between 160° and 200°, may be conveniently used for its preparation. On mixing gradually with concentrated potash and shaking, the reaction takes place with considerable evolution of heat, necessitating cooling; the epichlorhydrin separates to the surface as an oily layer, and is purified by fractional distillation. It is a limpid liquid, of sp. gr. 1·194 at 11°, and boils between 118° and 119°; it resembles chloroform in taste and smell.

Alcohol and ether dissolve it in all proportions. By long warming with water, in which it is insoluble, it combines with it to form monochlorhydrin.

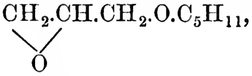
Epibromhydrin,  $\overset{O}{CH_2.CH}.CH_2Br$, isomeric with monobrom acetone, is very similar to the chlorine compound; it boils between 130° and 140°.

Epiiodo-hydrin, $C_3H_5I:O$, obtained by heating epichlorhydrin with potassic iodide, boils at about 160°.

Epiethylin, or *glyceryl oxy-ethyl ether*, prepared by the decomposition of ethyl chlorhydrin with alkali:

$$C_3H_5.Cl(OH).OC_2H_5 + OKH = KCl + OH_2 + C_3H_5(:O).OC_2H_5,$$

is a pleasantly smelling liquid, boiling between 126° and 130°.

Epichlorhydrin heated to 220° with isoamylic alcohol forms *isoamylchlor-hydrin*, $C_3H_5.Cl.(OH).(O.C_3H_{11})$, boiling at 235° and decomposing on distillation with concentrated alkali into *glyceryl oxide isoamyl ether*,  $\underset{O}{CH_2.CH}.CH_2.O.C_5H_{11}$, a mobile liquid of exceedingly pleasant odour, boiling at 188°.

687. Derivatives of glycerine are known, but not in the pure state, owing to difficulty of separation, bearing the same relation to glycerine that the poly-ethylene alcohols bear to ethylene glycol (§ 506).

They are generally formed by the abstraction of water from glycerine at a temperature of incipient decomposition.

When glycerine is saturated with HCl and heated with an equal volume of glycerine to 130°, a liquid is obtained distilling in a vacuum of 10 mm. between 220° and 230°, thus:

$$C_3H_5(OH)_3 + C_3H_5Cl(OH)_2 = HCl + C_3H_5(OH)_2.O.C_3H_5(OH)_2,$$

diglyceryl alcohol; and between 275° and 280° triglyceryl alcohol:

$$C_3H_5.(OH).[O.C_3H_5(OH)_2]_2,$$

passes over.

Salts of Glycerine with Inorganic Acids.

688. All or part of the hydroxylic hydrogen in glyceric hydrates may be substituted by acid radicals, neutral and basic compounds being known.

689. *Glyceric Nitrates.*—Glycerine dissolves in a mixture of fuming nitric acid and oil of vitriol with very considerable evolution of heat, the operation requiring to be gradually performed with strong cooling. On pouring the mixture into a large volume of water a heavy, colourless, poisonous oil, *glyceric trinitrate, nitro-glycerine,* $C_3H_5(O.NO_2)_3$, is precipitated. It crystallises at $-20°$ and has sp. gr. 1·6. In alcohol it is scarcely soluble, but easily in ether. Alcoholic potash saponifies it very easily into glycerine and potassic nitrate.

By percussion or quick heating nitro-glycerine explodes with fearful violence, complete combustion taking place, excess of oxygen being present, thus:

$$4C_3H_5(O.NO_2)_3 = 12CO_2 + 10H_2O + 6N_2 + O_2.$$

When merely inflamed, however, nitro-glycerine burns rapidly, but without explosion. It is much used as a blasting material either in the liquid form or mixed with silica or fine sand, generally then called *dynamite.* For purposes of transport it is often diluted with methyl alcohol.

Dichlorhydrin is converted by a mixture of nitric and sulphuric acids into *glyceryl dichlor-nitrate,* $CH_2Cl.CH(O.NO_2)CH_2Cl$, an oil boiling with decomposition between 180° and 190°, but not exploding; it has a sp. gr. at 10° of 1·465.

In a similar manner chlorbromhydrin gives

$$CH_2Cl.CH(O.NO_2)CH_2Br\ ;$$

epichlorhydrin, $CH_2Cl.CH(O.NO_2).CH_2.O.NO_2$. Both are thick liquids not distillable without decomposition. The latter is of sp. gr. 1·5112 at 9°.

690. Glycerine combines with sulphuric acid, when mixed with it, with evolution of a considerable amount of heat. On diluting with water and neutralising with chalk a mixture of calcic sulphate and the calcium salt of *sulpho-glyceric acid* is obtained; the latter may be separated from the gypsum by its much greater solubility in water.

The free acid may be obtained by exactly precipitating the calcium from a solution of the above salt with oxalic acid.

Glycerine sulphuric acid, or *sulpho-glyceric acid :*

$$C_3H_5(OH)_2(O.SO_2.OH),$$

is an acid and also a basic ether, and corresponds to monethyl sulphate or ethylene hydrate sulphate.

Its aqueous solution reacts strongly acid, and gives salts with oxides, and carbonates of basic metals mostly crystalline and without exception soluble in water.

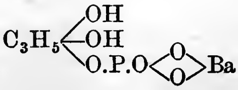
Monochlorhydrin similarly forms a chlorhydrin sulphuric acid, $C_3H_5Cl(OH).O.SO_2.OH$.

691. Powdered metaphosphoric acid mixed with glycerine also combines with it, forming *glycerine phosphoric acid :*

$$C_3H_5(OH)_2.O.PO.(OH)_2,$$

with evolution of heat.

On diluting with water and precipitating the excess of phosphoric acid with baric carbonate and then adding alcohol, baric glycero-phosphate:



$$C_3H_5\left\langle\begin{array}{l}OH\\OH\\O.P.O\left\langle\begin{array}{c}O\\O\end{array}\right\rangle Ba\end{array}\right.$$

is thrown down.

This salt, when decomposed by the exact quantity of sulphuric acid, yields the free acid, which on evaporation of its aqueous solution may be obtained in the form of an acid, thick syrup. Its salts are mostly soluble in water and crystallisable.

Its calcium salt is thrown down in pearly scales on boiling its cold saturated solution.

Glycerine phosphoric acid occurs as one of the decomposition products of *lecithin* (§ 697), and is physiologically important from its supposed existence in brain substance, &c.

Salts of Glycerine with Organic Acids. Fats.

692. Glycerine combines with the acids of the $C_nH_{2n-1}O.OH$ series when heated, water being eliminated. The number of hydroxyl groups replaced depends greatly on the temperature of the reaction and the quantity of acid present.

The neutral salts of the form $C_3H_5(O.C_nH_{2n-1}O)_3$ occur in most natural fats, and are in fact, in many, the principal substance. Most solid animal fats, *tallow*, &c., are composed of glycerine fats of palmitic and stearic acids. As yet no known fat consists entirely of the salt of one acid; they are generally mixtures of several, not only of the above-mentioned series, but also with salts of acids of the oleic series, $C_3H_5(O.C_nH_{2n-3}O)_3$. These latter salts confer liquidity (*animal oils*) or buttery consistency on many fats, according to the extent of their admixture.

Fatty or animal oils also frequently contain acids of still lower hydrogen contents, which oxidise easily on exposure to air, becoming hard and resinified, the same property being imparted in some degree to their glycerine salts, which are hence termed *drying oils*.

The existence of glycerine salts of mixed acids has no doubt a great influence in causing the variety of animal fats. It appears, for instance, that mutton fat, or sheep tallow, contains a glycerine distearin palmitate, $C_3H_5(O.C_{18}H_{35}O)_2.(O.C_{16}H_{31}O)$.

To extract fats from organic tissues or substance mechanical pressure, sometimes with elevation of temperature, is generally resorted to, whereby the cells containing the fats are broken. In cases where it is desired to extract the whole amount completely, solvents, like ether or disulphide of carbon, are used. From these the fat may be obtained by evaporation of the solvent.

Natural fats may be purified from the albuminous substances which generally accompany them, when mechanically extracted, by gently warming with a little potash solution or sulphuric acid, by which the albuminoids are decomposed or dissolved. Care must be taken that the temperature employed be not too high, or the glycerine salts or fats will themselves be saponified or converted by the sulphuric acid into free fatty acid and sulpho-glyceric acid.

The decomposition of fats by water or steam at a high temperature, as well as their decomposition by ammonia into glycerine and acid amides, has already been considered.

The fats, when heated by themselves, undergo dry distillation, acroleïn being one of the constant products, depending on the presence of glycerine in the fat.

693. Only one formic ether of glycerine is known—*glyceryl di-*

hydrate formate, or *monoformin,* $C_3H_5.(OH)_2(O.CHO)$. It is formed by heating glycerine with oxalic acid to 190°, and may be extracted from the cooled product of the reaction by ether, on the evaporation of which it remains as a colourless liquid, miscible with water and distilling unchanged in a vacuum. On heating to 200° it decomposes into CO_2, water, and allyl alcohol (§ 663).

694. *Acetic Acid Derivatives.*—Glycerine heated with glacial acetic acid for some time to a temperature of 100° yields a mixed product, from which ether extracts

Monacetin, or *glyceryl dihydrate acetate,* formed according to the equation:

$$C_3H_5(OH)_3 + HO.C_2H_3O = OH_2 + C_3H_5(OH)_2(O.C_2H_3O).$$

It is a colourless liquid, miscible with a small quantity of water, but is decomposed by a large quantity.

Diacetin, $C_3H_5.(OH).(O.C_2H_3O)_2$, is formed by heating glycerine with a large excess of acetic acid to 200°. It may also be extracted from the cooled reaction product by ether. It is a liquid, and boils at 280°.

Triacetin, glyceryl triacetate, $C_3H_5(O.C_2H_3O)_3$, obtained by long heating of diacetin with glacial acetic to about 250°, is a neutral oil of sp. gr. 1·174, boiling at 268°. It occurs naturally in small amount in the oil from the spindle tree (*Evonymus europaeus*).

695. In addition to the acetic ethers just mentioned, haloid acetates are also known.

Aceto-chlorhydrin, $C_3H_5Cl(OH)(O.C_2H_3O)$, prepared by the action of acetylic chloride on glycerine:

$$C_3H_5(OH)_3 + Cl.CO.CH_3 = H_2O + C_3H_5.Cl.(OH)C_2O_2H_3,$$

as a liquid of boiling point 250°.

Aceto-dichlorhydrin, $C_3H_5.Cl_2.(O.C_2H_3O)$, is formed, together with dichlorhydrin, by passing hydrochloric acid gas into a mixture of glycerine and glacial acetic acid heated to 100°; also from dichlorhydrin and acetyl chloride. There appears to be two isomers of this body, the one prepared in the former manner having a boiling point 205°, the latter, which is possibly $CH_2Cl.CH(O.C_2H_3O)CH_2Cl$, boiling at 194°–195°, and having sp. gr. 1·274 at 8°.

Both compounds give epichlorhydrin on saponification with potash:

$$C_3H_5.Cl_2(O.C_2H_3O) + 2KOH = KCl + KO.C_2H_3O + OH_2 \\ + C_3H_5(:O).Cl.$$

Diaceto-chlorhydrin, $C_3H_5Cl(OC_2H_3O)_2$, is best prepared by heating glycerine with acetic acid and acetyl chloride simultaneously. It boils about 245°.

Several corresponding bromine compounds are also known.

696. Analogous bodies to the acetins are produced by heating glycerine with the homologues of acetic acid. Many of these bodies have been prepared.

Tributyrin, $C_3H_5(O.CO.C_3H_7)_3$, occurs naturally in butter along with tricapronin, tricaprylin, tricaprinin, trilaurin, trimyrisin, tripalmitin, tristearin, and trioleïn.

Monopalmitin, $C_3H_5(OH_2)O.C_{16}H_{31}O)$, is solid, and melts at 58°; *dipalmitin*, $C_3H_5(OH)(C_{16}H_{31}O_2)_2$, at 59°; tripalmitin, $C_3H_5(C_{16}H_{31}O_2)_3$, at 63°. The latter is found in nearly all animal and vegetable fats. It is most easily obtained from olive oil, which is a mixture of that substance with trioleïn, $C_3H_5(O.C_{18}H_{33}O)_3$, by cooling, and pressing the solid palmitin from the liquid oleïn, and recrystallising from a mixture of alcohol and ether. It forms pearly plates difficultly soluble in alcohol. It melts about 46°.

Mono-, *di-*, and *tristearin* can be artificially prepared from stearic acid and glycerine. The latter is a very general constituent of natural fats, animal fats or tallows being composed principally of that body with a little tripalmitin and trioleïn.

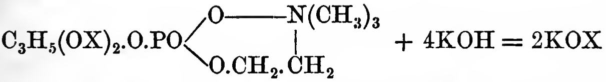
On treating tallow with cold ether, the two latter bodies may be extracted, most of the tristearin remaining behind. It may be dissolved and crystallised from warm ether, and got in pearly scales almost insoluble in cold alcohol and only very slightly so in warm ether. It melts at 63°. If it be not heated above 65° during the experiment it solidifies again at 61°, and then only melts again at 66°. If it be heated, however, higher than 67°, it solidifies again at 51°, and then melts at 53°, but returns to the melting point, 63°, after some time.

Other ethers occurring in natural fats will be considered under the respective acids.

697. *Lecithin.*—This name is applied to several bodies of very similar chemical and physical properties derived from brain substance, nerves, blood corpuscles, gall, &c., and also from some vegetable substances (maize, &c.), and which appear, indeed, as constant constituents of the cell substance of organised bodies. All these bodies, when decomposed by water, acids, or bases, give glycerine-phosphoric acid, neurine, and fatty acids.

Every lecithin is a fat containing only two fatty acid radicals, the third hydroxyl group being replaced by ethylen-trimethyl ammonic hydrate (neurine) in combination with phosphoric acid.

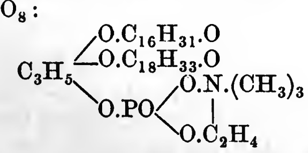
The following general formula, in which X may be supposed to represent the acid radicals of palmitic, stearic, and oleic acids, exhibits the constitution of lecithin, and the equation, its decomposition by alkalies:



$$C_3H_5(OX)_2.O.PO\begin{cases} O\text{———}N(CH_3)_3 \\ \qquad\quad | \\ O.CH_2.CH_2 \end{cases} + 4KOH = 2KOX$$

$$+ C_3H_5(OH)_2.O.PO(OK)_2 + HO.CH_2.CH_2.N.(CH_3)_3.OH.$$

Brain and nerve substance appear to contain the *palmitic oleic lecithin*, $C_{42}H_{82}NPO_8$:



$$C_3H_5\begin{cases} O.C_{16}H_{31}.O \\ O.C_{18}H_{33}.O \\ O.PO\begin{cases} O.N.(CH_3)_3 \\ \qquad | \\ O.C_2H_4 \end{cases} \end{cases}$$

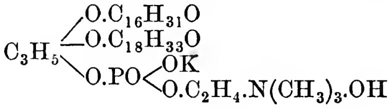
The preparation of lecithin from brain substance is only accomplished with great loss.

The brain substance must be freed as far as possible mechanically from blood vessels, cuticular substance, &c., rubbed up to a thin paste with water, and this repeatedly shaken out with ether, at a temperature of about 0°, until no more fat or cholesterine is taken up. The insoluble residue is then filtered from excess of water and pressed, after which it is heated with 80 % alcohol to between 40° and 45°. The warm alcoholic solution, after filtration and cooling, separates crude lecithin as a flocculent substance, which is again washed many times with ether to remove traces of fatty bodies, and finally crystallised from alcohol at a temperature of 45°. Lecithin may be obtained in a similar manner from amniotic liquid.

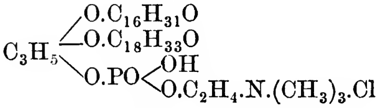
It can also be easily obtained from the latter substance by means of ether alcohol. After evaporating the ether and separating from the precipitated fats, an alcoholic solution of cadmic carbonate is added, which causes a precipitate of lecithin-cadmium chloride, which is suspended in water and treated with hydric sulphide. The lecithin hydrochloride thus set free is shaken out with ether, from which solution it is obtained by evaporation.

Lecithin crystallises from its saturated solution in alcohol in fine radially-grouped needles, which dry up in vacuo to a white powder, which melts on gently heating. It is slightly soluble in cold alcohol and ether, much more freely on heating. It may also be crystallised from glacial acetic acid.

With bases and acids compounds are formed on the type of



and



Sulphur Compounds of Glycerine.

698. *Mercaptans.*—Thio-hydrates of glyceryl are produced by the action of haloid glyceryl compounds on alcoholic solution of potassic sulph-hydrate according to the general equation :

$$C_3H_5.Cl_a(OH)_{3-a} + aKSH = aKCl + C_3H_5(SH)_a(OH)_{3-a},$$

in which a may have the values 1, 2, or 3. They have all the properties of the mercaptans proper, and exchange the hydrogen of their SH groups for mercury, copper, and similar metals.

Monosulph-hydrin, glyceryl thio-dioxyhydrate, $C_3H_5.(SH).(OH)_2$, obtained by double decomposition between monochlorhydrin and potassic sulph-hydrate, is a colourless, thick liquid, of sp. gr. 1·295 at 14°, which gives off a very disagreeable odour when warmed. It is only slightly soluble in water and not at all in ether.

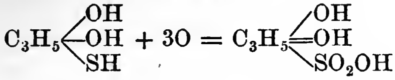
Disulph-hydrin, $C_3H_5(SH)_2OH$, obtained in a similar manner, only by using dichlorhydrin, has a sp. gr. = 1·342, and is insoluble in water and ether.

Trisulph-hydrin, $C_3H_5(SH)_3$, from trichlorhydrin. It is more liquid than glycerine, of sp. gr. 1·391, and only soluble in strong alcohol.

Glyceryl trisulphocyanate, $C_3H_5.(SCN)_3$, is the only sulphethereal salt of glycerine known. It may be prepared by the action of tribromhydrin on potassic sulphocyanate, and forms hard white needles melting at 126°.

699. *Sulphonic Acids.*—The glyceryl mercaptans pass on oxidation with nitric acid into sulphonic acids.

The reaction takes place pretty directly with the monosulph-hydrin, *glycerine monosulphonic acid*, which yields soluble and crystallisable salts, being formed :



$$C_3H_5{<}\begin{matrix}OH\\OH\\SH\end{matrix} + 3O = C_3H_5{<}\begin{matrix}OH\\OH\\SO_2OH\end{matrix}$$

Glycerine disulphonic acid is easily obtained in the form of potassic salt by boiling dichlorhydrin with a concentrated solution of neutral potassic sulphite :

$$C_3H_5(OH)Cl_2 + 2(K.SO_2OK) = 2KCl + C_3H_5(OH).(SO_2.OK)_2.$$

Trichlorhydrin yields in a similar manner the tribasic *glyceryl trisulphonic acid :*

$$C_3H_5Cl_3 + 3K.SO_2.OK = 3KCl + C_3H_5(SO_2.OK)_3.$$

Nitrogen Compounds of Glycerine.

700. Very few bodies of this class are known in a pure condition.

Although the haloid glycerine compounds, like the haloid combinations of all other alcohol radicals, act upon aqueous ammonia, the products, especially in the case of the di- and tri-substitution, are so numerous and complicated that a perfect separation becomes almost impossible.

As far as is known, however, they are basic compounds corresponding to the alkylamines.

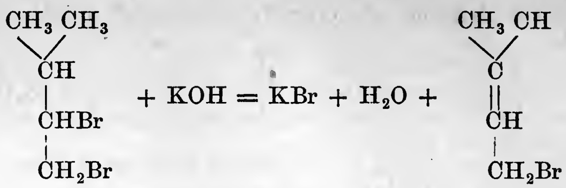
By heating dichlorhydrin with aqueous ammonia, the hydrochlorate of a *glyceramine*, or a basic substance which may either be glyceryl hydratamide, $C_3H_5(OH)_2NH_2$, or glyceryl oxide amide, $C_3H_5(:O).NH_2$, is formed along with ammonic chloride.

Homologues of Allyl and Glyceryl Derivatives.

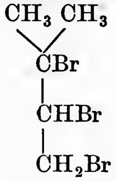
Homologues of the glyceryl compounds with four carbon atoms are not known as yet; several penta- and hexacarbon homologues are, however, known.

701. *Isoamyl Glycerine.*—Isoamylene dibromide is converted by strong alcoholic potash solution into potassic bromide and *bromisoamylene*, $C_5H_9.Br$. This latter is very probably a mixture of several isomeric bodies, and gives, on fractional distillation, a mobile oil, boiling between 100° and 110° and of not unpleasant odour.

Owing to its conversion, under the influence of hydrates, into a trihydric alcohol, the following formula appears most likely to express its constitution :



When carefully cooled and brought into contact with bromine, a *dimethacetyl bromide*, or *dimethglyceryl tribromide :*

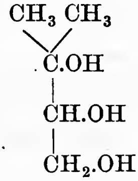


is produced, forming colourless elastic needles of camphor-like odour. It is soluble in ether and warm alcohol. Dimethyl-allyl bromide combines with chlorine to form *dimethyl-glyceryl brom-dichloride :*

$$(CH_3)_2 : CCl.CHCl.CH_2Br.$$

On heating the above isoamylene dibromide with potassic acetate in alcohol solution, a *brom-isoamylene diacetate*, $C_5H_9Br(O.C_2H_3O)_2$, is produced, which yields, on saponification, brom-isoamylene dihydrate, $C_5H_9Br(OH)_2$, from which the bromine may be removed by long heating with potassic hydrate, giving

Isoamyl glycerine, or *dimethyl glycerine :*



This is a thick liquid, soluble in water, and of a sweet, aromatic taste.

702. *Pseudo-Diallyl Alcohol.*—When diallyl is heated with hydric iodide, a compound of diallyl with two molecules of hydric iodide (§ 491, 2) is formed, and also a compound containing but one molecule of HI, thus :

$$CH_2 : CH.CH_2.CH_2.CH : CH_2 + HI$$
$$= CH_2 : CH.CH_2.CH_2.CHI.CH_3.$$

This iodide boils at 164°–165°, and is converted on heating with argentic acetate into the salt $CH_2 : CH.CH_2.CH(O.C_2H_3O)CH_3$ (boiling point 150°–160°), which gives on saponification *pseudo-diallyl alcohol,* $CH_2 : CH.CH_2.CH_2.CH(OH).CH_3$, an oily liquid boiling at 140° and of sp. gr. ·8625 at 0°.

The corresponding triatomic or trihydric alcohol :

$$CH_2(OH).CH(OH).CH_2.CH_2.CH(OH).CH_3,$$

has not yet been prepared.

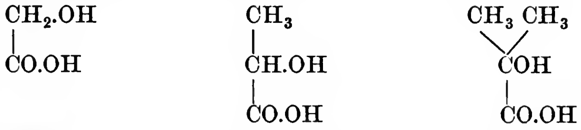
DERIVATIVES OF THE TETRAVALENT HYDROCARBON NUCLEI, C_nH_{2n-2}.

COMPOUNDS OF THE ALCOHOL ACID RADICALS, $\begin{array}{l} C_{n'}H_{2n'}- \\ | \\ C\equiv \end{array}$

703. By replacement by hydroxyl of one of the hydrogen atoms of the alcohol radical contained in a fatty acid, compounds are obtained which combine the characters of a monobasic acid with that of a monacid alcohol, the *hydroxy fatty acids:*

$$\begin{array}{l} C_{n'}H_{2n'}.OH \\ | \\ CO.OH \end{array}$$

According to the position of the hydroxyl on the carbon nucleus, primary, secondary, or tertiary alcohol acids are obtained:

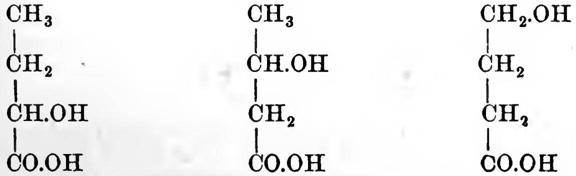


$$\begin{array}{l} CH_2.OH \\ | \\ CO.OH \end{array} \qquad \begin{array}{l} CH_3 \\ | \\ CH.OH \\ | \\ CO.OH \end{array}$$

Primary Secondary Tertiary

Alcohol acids.

If the nucleus contains three or more carbon atoms, the proximity or otherwise of the hydroxyl and carboxyl groups causes isomerism, which, according to the degree of proximity, are termed α-, β-, γ-, &c., derivatives:



$$\begin{array}{l} CH_3 \\ | \\ CH_2 \\ | \\ CH.OH \\ | \\ CO.OH \end{array} \qquad \begin{array}{l} CH_3 \\ | \\ CH.OH \\ | \\ CH_2 \\ | \\ CO.OH \end{array} \qquad \begin{array}{l} CH_2.OH \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CO.OH \end{array}$$

α- β- γ-

Hydroxy-butyric acids.

704. The alcohol and the acid hydroxyl groups can be replaced by other elements (halogens) or radicals (amides, &c.) in similar manner to the replacement of the hydroxyl groups of acids or alcohols; further, the hydrogen atoms can be replaced by metals and the radicals of acids and alcohols.

705. The following are amongst the most generally applicable methods of preparation :—

1. Those of the glycols which contain the primary alcohol group, $CH_2.OH$, at least once, are converted into hydroxy-acids on gentle oxidation, as by atmospheric oxygen in presence of platinum black or by dilute nitric acid :

$$C_nH_{2n}(OH).CH_2.OH + 2O = H_2O + C_nH_{2n}(OH).CO.OH.$$

2. The hydroxy-aldehydes (§§ 653 and 656) absorb oxygen from the air and reduce the oxides of noble metals :

$$C_nH_{2n}(OH).CO.H + O = C_nH_{2n}(OH).CO.OH.$$

3. The fatty acids yield mono-substitution products on heating with the halogens, and, when the nucleus contains at least three carbon atoms, give the α derivative in by far the greatest quantity :

$$\underset{\text{Propionic acid.}}{CH_3.CH_2.CO.OH} + Br_2 = HBr + \underset{\alpha\text{-Brom-propionic acid.}}{CH_3.CHBr.CO.OH.}$$

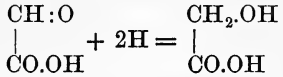
On long boiling the alkali salts of these latter, they decompose into metallic haloid and hydroxy-acid :

$$CH_2.Cl.CO.OK + HOH = KCl + CH_2(OH).CO.OH,$$

the process occurring in shorter time in presence of free alkali :

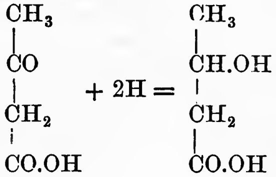
$$CH_2Cl.CO.OK + KOH = KCl + CH_2(OH).CO.OK.$$

4. The aldehyde and ketone acids derived from the pentavalent nucleus C_nH_{2n-3} (see later) combine with hydrogen and are converted into hydroxy-acids, the first into primary, the second into secondary alcohol acids :



$$\begin{array}{c}CH{:}O\\ |\\ CO.OH\end{array} + 2H = \begin{array}{c}CH_2.OH\\ |\\ CO.OH\end{array}$$

Aldehyde acid.

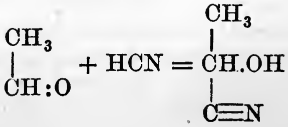


$$\begin{array}{c}CH_3\\ |\\ CO\\ |\\ CH_2\\ |\\ CO.OH\end{array} + 2H = \begin{array}{c}CH_3\\ |\\ CH.OH\\ |\\ CH_2\\ |\\ CO.OH\end{array}$$

Ketone acid.

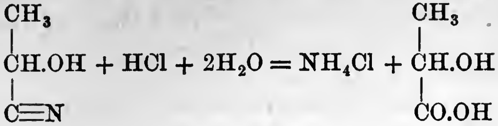
5. The aldehydes can be converted, with nucleus synthesis, in two ways into secondary α-alcohol acids.

a. Aldehydes unite directly with hydro-cyanic acid to form an *alkylidene hydrate cyanide :*



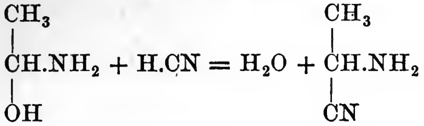
$$\begin{array}{c}CH_3\\ |\\ CH{:}O\end{array} + HCN = \begin{array}{c}CH_3\\ |\\ CH.OH\\ |\\ C{\equiv}N\end{array}$$

which, like all nitriles, is decomposed on warming with acids, yielding an ammonic salt and the secondary α-hydroxyl acid:



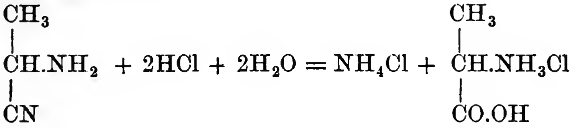
$$\begin{array}{l}CH_3\\ |\\ CH.OH\\ |\\ C\equiv N\end{array} + HCl + 2H_2O = NH_4Cl + \begin{array}{l}CH_3\\ |\\ CH.OH\\ |\\ CO.OH\end{array}$$

b. Aldehyde ammonias (§ 422) are readily converted into *alkylidene amid cyanides* by action of prussic acid:



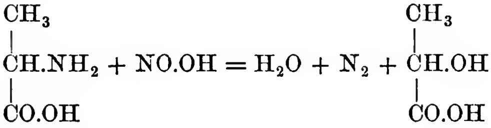
$$\begin{array}{l}CH_3\\ |\\ CH.NH_2\\ |\\ OH\end{array} + H.CN = H_2O + \begin{array}{l}CH_3\\ |\\ CH.NH_2\\ |\\ CN\end{array}$$

The latter are converted by dilute mineral acids into acid derivatives of *α-amidated fatty acids:*



$$\begin{array}{l}CH_3\\ |\\ CH.NH_2\\ |\\ CN\end{array} + 2HCl + 2H_2O = NH_4Cl + \begin{array}{l}CH_3\\ |\\ CH.NH_3Cl\\ |\\ CO.OH\end{array}$$

from which the secondary α-hydroxy-acid can be obtained by action of nitrous acid (comp. § 266):



$$\begin{array}{l}CH_3\\ |\\ CH.NH_2\\ |\\ CO.OH\end{array} + NO.OH = H_2O + N_2 + \begin{array}{l}CH_3\\ |\\ CH.OH\\ |\\ CO.OH\end{array}$$

The secondary α-hydroxy-acids are therefore *alkylidene hydrate carbonic acids:*

$$C_{n'}H_{2n'+1}.CH\left\{\begin{array}{l}OH\\ CO.OH\end{array}\right.$$

6. *Tertiary α-hydroxy-acids* can be prepared in similar manner from the ketones when a mixture of ketone and hydro-cyanic acid is decomposed by a mineral acid:

$$\begin{array}{l}CH_3\\ CH_3\end{array}\!\!>CO + HCN = \begin{array}{l}CH_3\\ CH_3\end{array}\!\!>C(OH).CN$$

$$\begin{array}{l}CH_3\\ CH_3\end{array}\!\!>C(OH).CN + HCl + 2H_2O = \begin{array}{l}CH_3\\ CH_3\end{array}\!\!>C(OH).CO.OH + NH_4Cl.$$

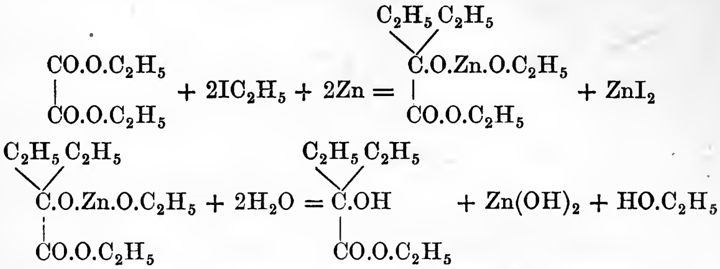
7. In similar manner to the formation of fatty acids from the alkyl haloids of next lower carbon contents the alcohol acids can be obtained from the olefine hydrate haloids (§ 493). The latter combine with potassic cyanide to *olefine hydrate cyanides:*

$$CH_2(OH).CH_2Cl + KCN = KCl + CH_2(OH).CH_2.CN,$$

and from these, *olefine hydrate carbonic acids*, which must be at least β-oxy-acids, are readily obtained :

$$CH_2(OH).CH_2.CN + HCl + 2OH_2 = CH_2(OH).CH_2.CO.OH + NH_4Cl.$$

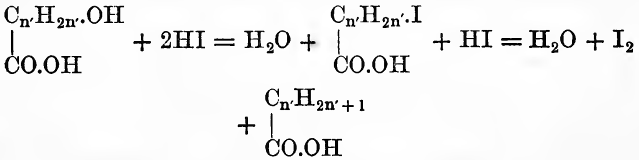
8. A method of very general application for the formation of tertiary α-alcohol acids consists in the decomposition of neutral ethereal oxalates with zinc dialkyls. If they are mixed together, or if the oxalate be heated with an alkyl iodide and zinc, and the product decomposed by water, the ethereal salt of a tertiary hydroxy-acid separates :



$$\begin{array}{l}CO.O.C_2H_5\\ |\\ CO.O.C_2H_5\end{array} + 2IC_2H_5 + 2Zn = \begin{array}{l}(C_2H_5)_2C.O.Zn.O.C_2H_5\\ |\\ CO.O.C_2H_5\end{array} + ZnI_2$$

$$\begin{array}{l}(C_2H_5)_2C.O.Zn.O.C_2H_5\\ |\\ CO.O.C_2H_5\end{array} + 2H_2O = \begin{array}{l}(C_2H_5)_2C.OH\\ |\\ CO.O.C_2H_5\end{array} + Zn(OH)_2 + HO.C_2H_5$$

706. On heating in sealed tubes with concentrated hydriodic acid the alcohol acids are reduced to the fatty acid of like carbon nucleus :



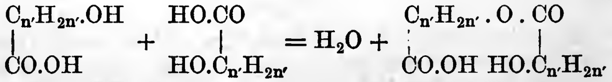
$$\begin{array}{l}C_{n'}H_{2n'}.OH\\ |\\ CO.OH\end{array} + 2HI = H_2O + \begin{array}{l}C_{n'}H_{2n'}.I\\ |\\ CO.OH\end{array} + HI = H_2O + I_2 + \begin{array}{l}C_{n'}H_{2n'+1}\\ |\\ CO.OH\end{array}$$

By dry distillation, or better by heating with dilute sulphuric acid, the α-hydroxy-acids are split up into formic acid and an aldehyde (secondary) or a ketone (tertiary) :

$$C_{n'}H_{2n'+1}.CH(OH).CO.OH = C_{n'}H_{2n'+1}.CH:O + H.CO.OH$$
$$(C_{n'}H_{2n'+1})_2.C(OH).CO.OH = (C_{n'}H_{2n'+1})_2CO + H.CO.OH.$$

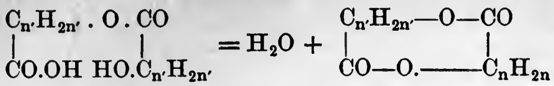
If oxidising agents are also present the formic acid is in great part converted into carbonic anhydride, the aldehyde into the corresponding fatty acid.

707. A peculiar property of the oxy-acids consists in their power to form two different ether-like derivatives when gently warmed with acids for some time, or by long standing in a perfectly dry atmosphere. Two molecules then so behave that one acts as an alcohol, the other as an acid :



$$\begin{array}{l}C_{n'}H_{2n'}.OH\\ |\\ CO.OH\end{array} + \begin{array}{l}HO.CO\\ \quad|\\ HO.C_{n'}H_{2n'}\end{array} = H_2O + \begin{array}{l}C_{n'}H_{2n'}.O.CO\\ |\qquad\qquad\quad|\\ CO.OH\ HO.C_{n'}H_{2n'}\end{array}$$

This *first ethereal anhydride* is at once both alcohol and monobasic acid, and is slowly decomposed by water into two molecules of the oxy-acid, or quickly by alkalies yielding salts of the latter. In dry vacuo, or on further careful heating, the first ethereal anhydride again loses water and gives the *second ethereal anhydride* :



$$\begin{array}{l} C_{n'}H_{2n'}\,.\,O\,.\,CO \\ |\qquad\qquad\ | \\ CO.OH\ \ HO.C_{n'}H_{2n'} \end{array} = H_2O + \begin{array}{l} C_{n'}H_{2n'}\text{—}O\text{—}CO \\ |\qquad\qquad\qquad\quad | \\ CO\text{—}O.\text{———}C_nH_{2n} \end{array}$$

which is also saponified by water and basic hydrates.

Glycollic Acid, $C_2H_4O_3$, and its Derivatives.

Compounds of the Radical Glycolyl, $—CH_2.C\equiv$.

708. The *tetrachloride* of this radical, $CH_2Cl.CCl_3$, is known, and has already been mentioned (§ 473), as *tetrachlor ethane*, obtained from ethane by direct chlorination. It is a colourless oil, which boils at 102°, and on heating with solution of potassic hydrate is converted into potassic glycollate :

$$CH_2Cl.CCl_3 + 5KOH = 4KCl + CH_2(OH).CO.OK + 2H_2O.$$

709. *Halogen-substituted acetic haloids* are obtained either from acetic chloride or bromide by action of free halogens :

$$CH_3.COCl + Cl_2 = HCl + CH_2Cl.COCl;$$

or by decomposition of glycollic acid or its salts by the phosphorus haloids :

$$CH_2(OH).CO.OH + 2PCl_5 = 2POCl_3 + 2HCl + CH_2Cl.COCl;$$

and finally from mono-halogen substitution derivatives of acetic acid by phosphorus haloids :

$$3CH_2Cl.CO.OH + PCl_3 = P(OH)_3 + 3CH_2Cl.COCl.$$

They unite the properties of alkyl haloids with those of the oxygenated acid radicals, and react with water to form substituted acetic acids :

$$CH_2Cl.COCl + H_2O = HCl + CH_2Cl.CO.OH.$$

Chlor-acetic chloride, $CH_2Cl.COCl$, chlorinated acetylic chloride, is a colourless fuming liquid of sp. gr. 1·495 at 0°, boiling at 105°.

Brom-acetic chloride, $CH_2Br.COCl$, is obtained from brom-acetic acid and phosphoric pentachloride as a liquid boiling at 134°. With water it yields hydrochloric acid and brom-acetic acid.

The isomeric *chlor-acetic bromide*, $CH_2Cl.COBr$, prepared from chlor-acetic acid and phosphoric bromide, also boils at 134°, but is decomposed by water into hydrobromic and chlor-acetic acids.

Brom-acetic bromide boils at 150°.

Halogen Substitution Derivatives of Acetic Acid.

710. These compounds, which stand in the same relation to glycollic acid as the alkyl haloids to the alcohols, are, as a rule, prepared from acetic acid or anhydride.

Chlor-acetic acid, $CH_2Cl.CO.OH$, is formed by the action of chlorine gas in sunlight on acetic acid heated to nearly the boiling point :

$$CH_3.CO.OH + Cl_2 = HCl + CH_2Cl.CO.OH.$$

Instead of operating in sunlight, some iodine can be dissolved in the acetic acid and chlorine then passed into the liquid. Iodine chloride is first formed, which reacts with the acetic acid, forming chlor-acetic and hydriodic acids; the latter, by action of further quantities of chlorine, yields hydrochloric acid and iodine chloride, which reacts anew on the acetic acid.

In this process some dichlor acetic acid is always formed, which can only be removed from the monochlor acid with difficulty; it is, therefore, more usual, by action of chlorine, to convert acetic anhydride into acetic chloride and chlor-acetic acid (§ 624), and to then separate the products by fractional distillation.

Chlor-acetic acid crystallises in rhombic tables or prisms, melting at 62° and boiling at 185°–187°. They have a caustic action on the skin and deliquesce in air. The salts are mostly readily soluble in water and crystallisable. The potassic salt, $CH_2Cl.CO.OK$, separates in nacreous plates on neutralising a cold alcoholic solution of potassic hydrate with one of the acid. An acid potassic salt:

$$CH_2Cl.CO.OK,CH_2Cl.CO.OH,$$

is also known. On addition of argentic nitrate to a concentrated solution of the neutral potassic salt, a scaly precipitate of argentic chloracetate, $CH_2Cl.CO.OAg$, is formed, which detonates when heated to 120° in the dry state. All its salts are decomposed on boiling with water, glycollic acid being formed (§ 705, 3).

Ethylic chlor-acetate, $CH_2Cl.CO.O.C_2H_5$, is formed by saturating a solution of one part of chlor-acetic acid in four to five parts of alcohol with hydrochloric acid. After standing for twenty-four hours, ethylic chloride and the greater part of the alcohol are removed by distillation from the water bath, and the cooled residue mixed with several times its volume of water. The lower oily layer is then washed several times with water, dried over calcic chloride, and purified by distillation. It is also obtained by the careful addition of acetic chloride to ethylic alcohol:

$$CH_2Cl.COCl + HO.C_2H_5 = HCl + CH_2Cl.CO.O.C_2H_5.$$

It is a colourless, mobile liquid, heavier than water, boiling at 143°–144°, and whose vapours attack the eye violently.

711. *Brom-acetic acid*, $CH_2Br.CO.OH$, is best obtained by heating equal molecules of bromine and glacial acetic acid to 120°–130° in strong sealed glass tubes. It crystallises in colourless, readily fusible rhombohedra, and boils at 208°. Its ethylic salt, $CH_2Br.CO.O.C_2H_5$, boils with partial decomposition at 159°.

Iod-acetic acid, $CH_2I.CO.OH$. On heating an alcoholic solution of ethylic brom-acetate with potassic iodide, ethylic iod-acetate is formed, which is separated on addition of water as a brown oil which cannot be distilled without decomposition. This is readily saponified by solution of baric hydrate, and the resulting baric salt, on treatment with the requisite quantity of sulphuric acid, gives a solution of iod-acetic acid. On evaporating this in vacuo, iod-acetic acid is left in colourless rhombic tables, which melt at 82° and decompose at higher temperatures. It is readily soluble in water, but does not deliquesce in air. The silver salt readily decomposes in presence of water into argentic iodide and glycollic acid. By heating with concentrated hydriodic acid it is converted into acetic acid.

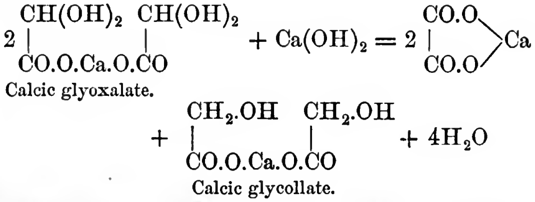
Glycollic Acid.

712. *Glycollic acid, hydroxy-acetic acid,* or *methene hydrate carbonic acid,* $CH_2(OH).CO.OH$, was first obtained by oxidation of an aqueous solution of glycocine acid with nitrous acid.

It is further formed by the oxidation of ethylene glycol by air and platinum black:

$$CH_2(OH).CH_2.OH + 2O = CH_2(OH).CO.OH + H_2O.$$

In large quantity it is prepared by the oxidation of ethylic alcohol with nitric acid. 100 grams of 80 % alcohol are placed in a glass cylinder, at most 5 c.m. wide. 50 grams of water are then added by means of a funnel tube drawn to a capillary point, so as to form a layer below the alcohol, and then 170 grams of nitric acid, of sp. gr. 1·35, similarly poured in, forming a layer below the water. The three layers mix, on quiet standing (in about five days at 20°–22°), with oxidation of the alcohol and evolution of gas. The homogeneous liquid is then evaporated in small portions to a syrup on the water bath, and this—a mixture of oxalic, glyoxalic, and glycollic acids and glyoxal—after dilution with ten times its volume of water, neutralised at the boiling temperature with powdered chalk. On cooling, the whole becomes a stiff pulp of crystals, which is mixed with an equal bulk of alcohol, strained and pressed. The alcoholic filtrate serves for the preparation of glyoxal. The mixture of calcic salts is boiled with water and filtered boiling; calcic oxalate remains undissolved; the cooled filtrate deposits first calcic glyoxalate, or a double compound of it, with calcic glycollate, whilst the greater part of the latter remains in the mother liquor. In order to remove the slight portion of glyoxalate still remaining in solution, the mother liquor is boiled with calcic hydrate:



$$2\begin{array}{l}\mathrm{CH(OH)_2}\quad \mathrm{CH(OH)_2}\\ |\qquad\qquad\qquad |\\ \mathrm{CO.O.Ca.O.CO}\end{array} + \mathrm{Ca(OH)_2} = 2\begin{array}{l}\mathrm{CO.O}\\ |\\ \mathrm{CO.O}\end{array}\!\!>\mathrm{Ca} + \begin{array}{l}\mathrm{CH_2.OH}\quad \mathrm{CH_2.OH}\\ |\qquad\qquad\qquad |\\ \mathrm{CO.O.Ca.O.CO}\end{array} + 4H_2O$$

Calcic glyoxalate.

Calcic glycollate.

and the filtered solution evaporated. Glycollic acid is then liberated by precipitation of the calcium with oxalic acid.

Glycollic acid is prepared from chlor-acetic acid by slightly overneutralising an aqueous solution of the latter with potassic hydrate and then heating to boiling for a long time. Whenever an acid reaction is observed a slight excess of alkali is added, until the reaction of the liquid remains faintly alkaline after long boiling. It then contains potassic chloride and potassic glycollate. After slight acidulation with sulphuric acid, cupric sulphate is added, and the mixture allowed to stand some days, when green crusts of the difficultly soluble cupric glycollate separate, which is readily obtained chemically pure by recrystallisation from boiling water. The boiling aqueous solution is then decomposed by hydric sulphide, filtered from cupric sulphide, and evaporated to a syrup on the water bath.

On standing in a desiccator the syrupy glycollic acid solidifies after a time to a colourless, indistinctly crystalline mass, melting at 80° and deliquescing in air. It is a strong acid, and is readily soluble in alcohol and ether.

On long heating to 100° the greater part volatilises, leaving some glycollide (§ 713).

By heating with sulphuric acid it is decomposed into formic acid and formic aldehyde, the latter appearing as paraformic aldehyde, and the formic acid in great part splitting up into water and carbonic oxide:

$$3CH_2(OH).CO.OH. = (CH_2:O)_3 + 3HCO.OH.$$

Oxidising agents readily convert it into oxalic acid, glyoxalic acid probably being formed as an intermediate product.

By heating with hydrochloric or hydrobromic acids it is reconverted into chlor or brom acetic acid:

$$CH_2(OH).CO.OH + HCl = CH_2Cl.CO.OH + H_2O,$$

whilst hydriodic acid converts it into acetic acid.

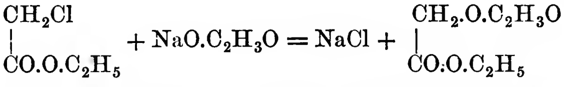
Phosphoric chloride converts it into chlor-acetic chloride (§ 709).

The alkali salts of glycollic acid are extremely soluble. The *calcic salt*, $[CH_2(OH).CO.O]_2Ca,4H_2O$, crystallises in fine needles, which dissolve in 82 parts of water at 10° and in 19 parts at 100°. Argentic glycollate, $[CH_2(OH).CO.OAg]_2,H_2O$, is a crystalline precipitate which dissolves, with blackening, in boiling water.

Ethereal Salts of Glycollic Acid.

712*a*. These compounds are obtained by heating glycollide with the monacid alcohols. *Ethylic glycollate*, $CH_2(OH)CO.O.C_2H_5$, is a neutral liquid, boiling at 150°, is miscible with water and readily saponifiable by alkalies.

Salts are also obtainable in which glycollic acid plays the part of the base, as in *aceto-glycollic acid.* By heating ethylic chlor-acetate with anhydrous sodic acetate there is obtained *ethylic* aceto-glycollate:



$$\begin{matrix} CH_2Cl \\ | \\ CO.O.C_2H_5 \end{matrix} + NaO.C_2H_3O = NaCl + \begin{matrix} CH_2.O.C_2H_3O \\ | \\ CO.O.C_2H_5 \end{matrix}$$

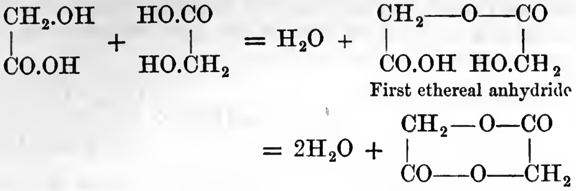
as a thin oil of agreeable fruity odour, boiling at 179°. If two molecules of this are mixed with not quite one molecule of calcic hydrate, calcic aceto-glycollate is obtained:

$$2C_2H_3O.O.CH_2.CO.O.C_2H_5 + Ca(OH)_2 = 2HO.C_2H_5 + (C_2H_3O.O.CH_2.CO.O)_2Ca,$$

which on evaporation of the solution is obtained in prismatic crystals. By boiling with excess of base, the methene-acetate group is readily saponified:

$$(C_2H_3O.O.CH_2.CO.O)_2Ca + Ca(OH)_2 = (C_2H_3O.O)_2Ca + (HO.CH_2.CO.O)_2Ca.$$

713. Both the *ethereal anhydrides* (§ 707) of glycollic acid are known. By long fusion on the water bath, or by contact with the vapours of sulphuric anhydride, glycollic acid is converted, with loss of water, into an amorphous mass, insoluble in water, the *first ethereal anhydride*, which fuses at 128°–130° and on long heating yields, with partial volatilisation, the *second ethereal anhydride, glycollide :*



$$\begin{array}{l} CH_2.OH \\ | \\ CO.OH \end{array} + \begin{array}{l} HO.CO \\ \quad | \\ HO.CH_2 \end{array} = H_2O + \begin{array}{l} CH_2—O—CO \\ | \qquad\qquad\quad | \\ CO.OH\ HO.CH_2 \end{array}$$

First ethereal anhydride

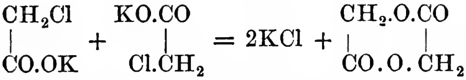
$$= 2H_2O + \begin{array}{l} CH_2—O—CO \\ | \qquad\qquad\quad | \\ CO—O—CH_2 \end{array}$$

Second ethereal anhydride.

Glycollide was first obtained by heating tartronic acid to 180° :

$$2C_3H_4O_5 = 2CO_2 + 2H_2O + C_4H_4O_4,$$

but is most readily obtained by long heating of potassic chlor-acetate at 150° :

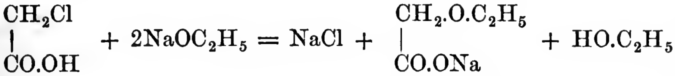


$$\begin{array}{l} CH_2Cl \\ | \\ CO.OK \end{array} + \begin{array}{l} KO.CO \\ \quad | \\ Cl.CH_2 \end{array} = 2KCl + \begin{array}{l} CH_2.O.CO \\ | \qquad\quad | \\ CO.O.CH_2 \end{array}$$

It is an amorphous mass, which on long boiling with water dissolves to glycollic acid, and which with two molecules of alkali quickly saponifies to glycollates.

Ethereal Derivatives of Glycollic Acid.

714. These compounds, in which the hydroxylic hydrogen atom of the alcohol group is replaced by an alcohol radical, are obtained by double decomposition between an alkaline chlor-acetate and a sodic alkylate, when one molecule of the chlor-acetic acid is employed to two atoms of sodium dissolved in the respective alcohol, the mixture being heated at the end of the violent reaction :



$$\begin{array}{l} CH_2Cl \\ | \\ CO.OH \end{array} + 2NaOC_2H_5 = NaCl + \begin{array}{l} CH_2.O.C_2H_5 \\ | \\ CO.ONa \end{array} + HO.C_2H_5$$

Sodic chloride separates whilst the sodic salt of the alkyl glycollic acid remains dissolved in the excess of alcohol, from which it can be precipitated by addition of ether. The *alkyl glycollic acid* can be liberated by addition of sulphuric acid.

Methyl glycollic acid, $CH_3.O.CH_2.CO.OH$, or *methoxyacetic acid*, is a colourless, thick, strongly acid liquid of sp. gr. 1·18 and boiling point 198°. Its alkali salts are deliquescent, but crystallisable, the calcic salt amorphous; the readily soluble zinc and copper salts crystallise beautifully with two molecules of water :

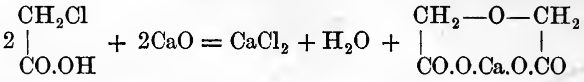
$$(CH_3.O.CH_2.CO.O)_2Zn,2H_2O.$$

Ethyl glycollic acid, $C_2H_5.O.CH_2.CO.OH$, or *ethoxyacetic acid*, isomeric with ethylic glycollate, boils at 190°, its ethylic salt,

$C_2H_5O.CH_2.CO.O.C_2H_5$, at 155°. The latter, on saponification with alkalies, yields alkaline ethyl glycollates.

Isoamyl glycollic acid boils at 235°.

714*a*. In addition to the above bodies, which correspond to the mixed ethers, the *simple ether anhydride* of glycollic acid—*diglycollic acid*—$O(CH_2.CO.OH)_2$, is also known, and is isomeric with the first ethereal anhydride. It is obtained, together with glycollic acid, by boiling chlor-acetic acid with bases, the yield being especially rich on employment of milk of lime:



$$2\begin{array}{l}CH_2Cl\\|\\CO.OH\end{array} + 2CaO = CaCl_2 + H_2O + \begin{array}{l}CH_2—O—CH_2\\|\qquad\qquad\quad|\\CO.O.Ca.O.CO\end{array}$$

The difficultly soluble calcic salt separates from the solution in crystals, leaving calcic glycollate in solution, and may be decomposed by oxalic or sulphuric acids.

Diglycollic acid is also obtained by oxidation of diethylene alcohol with nitric acid. It forms large transparent rhombic crystals, which dissolve readily in water and alcohol and melt at 148°. It is a dibasic acid, yielding acid and normal salts:

$$O\begin{array}{l}.CH_2.CO.OH\\.CH_2.CO.OK\end{array} \qquad O\begin{array}{l}.CH_2.CO.OK\\.CH_2.CO.OK\end{array}$$

As an ether diglycollic acid is not decomposed by boiling with excess of alkali; excess of phosphoric chloride converts it into chlor-acetic chloride:

$$HO.CO.CH_2.O.CH_2.CO.OH + 3PCl_5 = 3POCl_3 + 2HCl$$
$$+ 2Cl.CH_2.COCl.$$

By heating ethylic chlor-acetate with dried sodic carbonate *diglycollic ethyl-ether* is obtained:

$$2ClCH_2.CO.O.C_2H_5 + Na_2CO_3 = 2NaCl + CO_2$$
$$+ O(CH_2.CO.O.C_2H_5),$$

as a colourless oil, heavier than water, which boils at 240° and yields salts of diglycollic acid on saponification.

The acid anhydride of glycollic acid, $HO.CH_2.CO.O.CO.CH_2.OH$, has not yet been prepared.

Sulphur Derivatives of Glycollic Acid.

715. *Thio-glycollic Acid.*—Of the possible isomeric thio-glycollic acids, $CH_2(SH)CO.OH$ and $CH_2(OH).CO.SH$, only the first, *mercapto-glycollic acid*, has been prepared by heating potassic chlor-acetate with potassic sulph-hydrate:

$$Cl.CH_2.CO.OK + HSK = KCl + HS.CH_2.CO.OK.$$

It is best separated by treatment of the amorphous difficultly soluble lead salt with hydric sulphide, and is then obtained on evaporation of the aqueous solution as a nearly solid, yellow, deliquescent mass, of strongly acid reaction.

The ethylic salt, $HS.CH_2.CO.O.C_2H_5$, is readily prepared by boiling the acid with alcohol and some hydrochloric acid. It behaves as a true mercaptan, e.g. yields the crystalline mercury compounds:

$$Cl.Hg.S.CH_2.CO.O.C_2H_5 \text{ and } Hg(S.CH_2.CO.O.C_2H_5)_2,$$

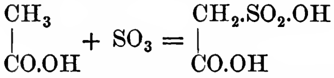
and is readily oxidised by nitric acid to *sulphonacetic acid.*

Thio-diglycollic acid, $S(CH_2.CO.OH)_2$, is formed by heating chloracetic acid with potassic sulphide; its ethylic salt, $S(CH_2.CO.O.C_2H_5)_2$, a yellow oil boiling at 267°, is formed, together with mercapto-glycollic acid, by heating ethylic chlor-acetate with an alcoholic solution of potassic sulph-hydrate:

$$\begin{array}{l} Cl.CH_2.CO.O.C_2H_5 + HSK = KCl + HS.CH_2.CO.O.C_2H_5 \\ HS.CH_2.CO.O.C_2H_5 + HSK = KS.CH_2.CO.O.C_2H_5 + H_2S \\ KS.CH_2.CO.O.C_2H_5 + Cl.CH_2.CO.O.C_2H_5 = KCl \\ \qquad\qquad + S(CH_2.CO.O.C_2H_5). \end{array}$$

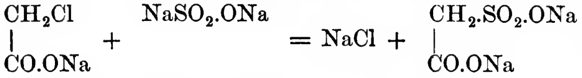
The acid is solid and crystallises in readily soluble rhombic tables, melting at 129°.

715*a*. *Sulphonacetic acid,* $CH_2(SO_2.OH).CO.OH$, or *sulpho-acetic acid,* has already been mentioned as an oxidation product of mercapto-glycollic acid; it is further formed by bringing together acetic acid and sulphuric anhydride (comp. § 513):



$$\begin{array}{l} CH_3 \\ | \\ CO.OH \end{array} + SO_3 = \begin{array}{l} CH_2.SO_2.OH \\ | \\ CO.OH \end{array}$$

and by boiling an alkaline chlor-acetate with neutral sodic sulphite:



$$\begin{array}{l} CH_2Cl \\ | \\ CO.ONa \end{array} + NaSO_2.ONa = NaCl + \begin{array}{l} CH_2.SO_2.ONa \\ | \\ CO.ONa \end{array}$$

By addition of sulphuric acid to the baric salt:

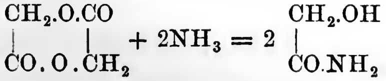
$$CH_2\left\{\begin{array}{l} SO_2O. \\ CO.O. \end{array}\right. Ba, H_2O,$$

it is obtained in the free state, and then forms colourless, deliquescent prisms, melting at 62°–63°. Its salts are soluble in water. By heating with excess of sulphuric anhydride it is converted into methene disulphonic acid (§ 419):

$$CH_2\left\{\begin{array}{l} SO_2.OH \\ CO.OH \end{array}\right. + SO_3 = CH_2\left\{\begin{array}{l} SO_2.OH \\ SO_2.OH \end{array}\right. + CO_2$$

Amine Derivatives of Glycollic Acid.

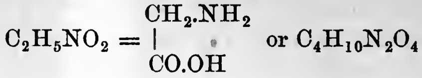
716. *Glycolamide,* $C_2H_5NO_2 = CH_2(OH).CO.NH_2$, is obtained by the action of ammonia on the ethereal salts of glycollic acid, and also by heating glycollide in an atmosphere of ammonia gas:



$$\begin{array}{ll} CH_2.O.CO & \\ | & | \\ CO.O.CH_2 & \end{array} + 2NH_3 = 2 \begin{array}{l} CH_2.OH \\ | \\ CO.NH_2 \end{array}$$

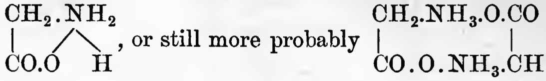
It forms colourless crystals, melting at 120°, which yield ammonic glycollate on boiling with water, and are decomposed by alkalies into ammonia and glycollates.

717. *Glycocine, glycocoll,* or *amido-acetic acid:*



$$C_2H_5NO_2 = \begin{array}{l} CH_2.NH_2 \\ | \\ CO.OH \end{array} \quad \text{or } C_4H_{10}N_2O_4$$

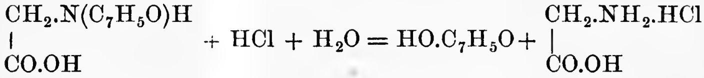
is isomeric with glycollamide. As it is at once an amine and an acid, its true composition is in all probability that of a salt:



$$\begin{array}{l} CH_2.NH_2 \\ |\quad / \backslash \\ CO.O\quad H \end{array}, \text{ or still more probably } \begin{array}{l} CH_2.NH_3.O.CO \\ |\qquad\qquad\quad | \\ CO.O.NH_3.CH_2 \end{array}$$

this view being in complete accordance with its properties.

Prior to the discovery of glycollic acid glycocine had already been obtained from different animal substances by boiling with mineral acids or alkalies—e.g. from gelatine (hence the name glycocine = sugar of gelatine), from hippuric acid, and, together with taurocholic acid (comp. § 528), from the glycocholic acid occurring in the gall. It is most readily obtained from hippuric acid (benzoyl glycocoll), contained in large quantity in the urine of herbivora, by boiling for some hours with concentrated hydrochloric acid. The solution is evaporated nearly to dryness, and the pulpy residue extracted with a little cold water, which takes up glycocine hydrochloride and leaves the resulting benzoic acid nearly untouched:

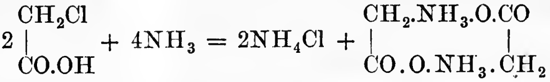


$$\begin{array}{l} CH_2.N(C_7H_5O)H \\ | \\ CO.OH \end{array} + HCl + H_2O = HO.C_7H_5O + \begin{array}{l} CH_2.NH_2.HCl \\ | \\ CO.OH \end{array}$$

Hippuric acid. Benzoic acid. Glycocine hydrochloride.

The solution is then boiled with plumbic hydrate, filtered from the precipitated plumbic oxychloride, treated with hydric sulphide to remove lead, and evaporated to crystallisation.

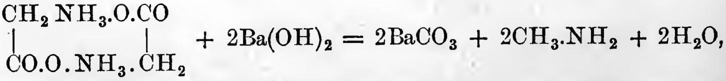
It is obtained synthetically by heating chlor or brom acetic acid with ammonia:



$$2 \begin{array}{l} CH_2Cl \\ | \\ CO.OH \end{array} + 4NH_3 = 2NH_4Cl + \begin{array}{l} CH_2.NH_3.O.CO \\ |\qquad\qquad\quad | \\ CO.O.NH_3.CH_2 \end{array}$$

but, as in the preparation of the alkylamines, the process goes in part further, diglycollamic acid and triglycollamic acid being formed.

Glycocine forms large, hard, monoclinic prisms, unalterable in air, of strongly sweet taste and neutral reaction, which dissolve in four times their weight of cold water, but little in alcohol and not at all in ether. It melts at 170°, and decomposes at slightly higher temperature with carbonisation and formation of ammonia and some methylamine. The latter is especially formed on heating with baric hydrate:



$$\begin{array}{l} CH_2\,NH_3.O.CO \\ |\qquad\qquad\quad | \\ CO.O.NH_3.CH_2 \end{array} + 2Ba(OH)_2 = 2BaCO_3 + 2CH_3.NH_2 + 2H_2O,$$

but not on employment of alkalies, which only give ammonia (comp. § 16).

Nitrous acid converts glycocine into glycollic acid.

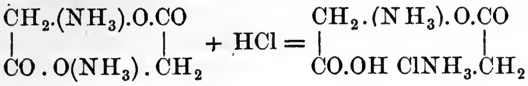
718. As organic ammonic salt glycocine is altered by strong acids, bases, or the salts of both.

By treatment with strong mineral acids glycocine salts are formed, which being at the same time free organic acids, have an acid reaction. These reactions occur in two stages.

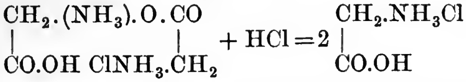
On dissolving a molecule of glycocine ($C_4H_{10}N_2O_4$) in a molecule of hydrochloric acid, colourless prisms of the formula :

$$C_4H_{10}N_2O_4.HCl,$$

crystallise on cooling, which, with excess of acid, yield the very soluble compound $C_2H_5NO_2.HCl$:



$$\begin{array}{l} \mathrm{CH_2.(NH_3).O.CO} \\ | \qquad\qquad\qquad | \\ \mathrm{CO.O(NH_3).CH_2} \end{array} + \mathrm{HCl} = \begin{array}{l} \mathrm{CH_2.(NH_3).O.CO} \\ | \qquad\qquad\qquad | \\ \mathrm{CO.OH\ ClNH_3.CH_2} \end{array}$$



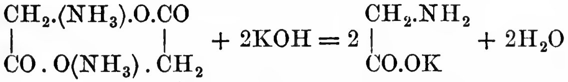
$$\begin{array}{l} \mathrm{CH_2.(NH_3).O.CO} \\ | \qquad\qquad\qquad | \\ \mathrm{CO.OH\ ClNH_3.CH_2} \end{array} + \mathrm{HCl} = 2 \begin{array}{l} \mathrm{CH_2.NH_3Cl} \\ | \\ \mathrm{CO.OH} \end{array}$$

The latter gives with platinic chloride a readily soluble, crystalline double salt, $(HO.CO.CH_2.NH_3Cl)_2,PtCl_4$. The sulphate

$$(HO.CO.CH_2.NH_3)_2SO_4$$

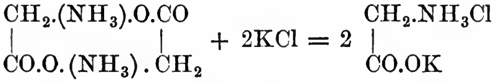
crystallises with difficulty.

Strong basic hydrates give salts of alkaline reaction which are at the same time free amine bases :



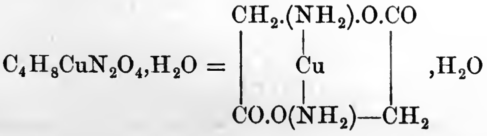
$$\begin{array}{l} \mathrm{CH_2.(NH_3).O.CO} \\ | \qquad\qquad\qquad | \\ \mathrm{CO.O(NH_3).CH_2} \end{array} + 2\mathrm{KOH} = 2 \begin{array}{l} \mathrm{CH_2.NH_2} \\ | \\ \mathrm{CO.OK} \end{array} + 2\mathrm{H_2O}$$

Glycocine yields with many neutral salts compounds which generally crystallise beautifully, to whose formation both the above-mentioned reactions combine :



$$\begin{array}{l} \mathrm{CH_2.(NH_3).O.CO} \\ | \qquad\qquad\qquad | \\ \mathrm{CO.O.(NH_3).CH_2} \end{array} + 2\mathrm{KCl} = 2 \begin{array}{l} \mathrm{CH_2.NH_3Cl} \\ | \\ \mathrm{CO.OK} \end{array}$$

719. Weak basic metallic oxides or hydrates are also taken up by glycocine. They are mostly the oxides of metals which readily replace the hydrogen of ammonia and amides, such as copper, mercury, and silver. The resulting crystallisable compounds are therefore probably not analogous to those of the alkalies. Especially characteristic is the cupric compound, obtained by boiling a solution of glycocine with cupric oxide, which separates from the deep blue liquid in beautiful blue needles of the formula :



$$\mathrm{C_4H_8CuN_2O_4,H_2O} = \begin{array}{l} \mathrm{CH_2.(NH_2).O.CO} \\ | \qquad\quad | \qquad\quad | \\ | \qquad\ \mathrm{Cu} \qquad | \\ | \qquad\quad | \qquad\quad | \\ \mathrm{CO.O(NH_2)—CH_2} \end{array} ,\mathrm{H_2O}$$

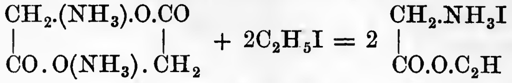
Their water of crystallisation is lost at 100°. The analogous silver compound, $C_4H_8Ag_2N_2O_4$, separates in colourless anhydrous crystals.

From these bodies the metal in union with nitrogen *cannot* be precipitated by alkalies. Copper glycocine dissolves in alkali solutions with deep blue colour, a compound of the formula :

$$Cu(NH.CH_2.CO.OK)_2,$$

doubtless being formed.

On heating an alcoholic solution of glycocine with ethylic iodide to about 120°, *ethylic glycocine hydro-iodide* is formed :



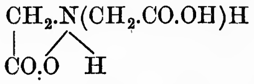
$$\begin{matrix} CH_2.(NH_3).O.CO \\ | \qquad\qquad | \\ CO.O(NH_3).CH_2 \end{matrix} + 2C_2H_5I = 2 \begin{matrix} CH_2.NH_3I \\ | \\ CO.O.C_2H \end{matrix}$$

It remains on evaporation in colourless, rhombic crystals, which are also readily soluble in water or ether. On shaking the aqueous solution with argentic oxide, hydriodic acid is removed, but on evaporating the *ethylic amido-acetate*, $NH_2.CH_2.CO.O.C_2H_5$, is decomposed by the water into glycocine and ethylic alcohol.

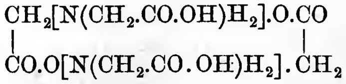
720. *Diglycollamic Acid and Triglycollamic Acid.*—As already mentioned, these are formed in the preparation of glycocine from chloracetic acid and excess of ammonia. The resulting solution contains, in addition to ammonic chloride and glycocine, the ammonic salts of diglycollamic and triglycollamic acids. By evaporation the greater part of the ammonic chloride is removed, and the mother liquid is then boiled with plumbic hydrate until all ammonia is driven off. Plumbic triglycollamate separates, whilst the filtered solution contains glycocine and plumbic diglycollamate. This is then treated with hydric sulphide to remove lead, and boiled with zincic carbonate in order to separate diglycollamic acid as its difficultly soluble zinc salt.

Diglycollamic acid, $C_4H_7NO_4$, crystallises in large, colourless, rhombic prisms, not perceptibly soluble in cold water, insoluble in alcohol and ether. It tastes and reacts acid, and behaves towards carbonates as a monobasic acid, but by treatment with strong basic hydrates takes up two equivalents of metal.

It is glycocine, in which the nitrogen is united to the methene carbonic acid residue of glycollic acid, $CH_2.CO.OH$, in place of a hydrogen atom ; therefore

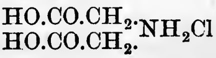


or probably



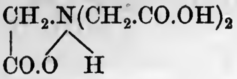
$$\begin{matrix} CH_2[N(CH_2.CO.OH)H_2].O.CO \\ | \qquad\qquad\qquad\qquad\qquad | \\ CO.O[N(CH_2.CO.OH)H_2].CH_2 \end{matrix}$$

With strong acids it yields crystallisable salts similar to glycocine, e.g.

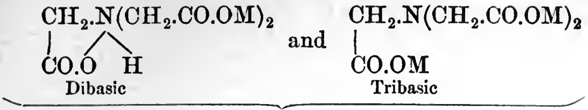


$$\begin{matrix} HO.CO.CH_2. \\ HO.CO.CH_2. \end{matrix} NH_2Cl$$

Triglycollamic acid, $C_6H_9NO_6$, crystallises in very difficultly soluble small prisms. It is glycocine with two methene carbonic acid groups on each nitrogen atom, and unites with carbonates to dibasic, with free bases to tribasic, salts :



Triglycollamic acid
(probably with doubled formula).

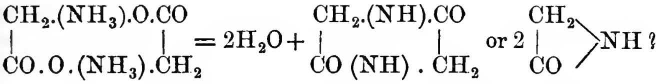


Salts.

Mineral acids do not unite with it.

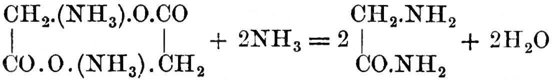
On treatment of the tribasic silver salt with ethylic iodide, *triethylic triglycollamate*, $N(CH_2CO.O.C_2H_5)_3$, is obtained as an oily liquid, very little soluble in water, which boils at 290° with partial decomposition, and unites with ammonia, forming *triglycollamic triamide*, $N(CH_2.CO.NH_2)_3$. This latter crystallises in difficultly soluble tables ; these, on boiling with water, are converted into free ammonia and the dibasic ammonic salt, and yield a crystalline salt with hydrochloric acid, $N(CH_2.CO.NH_2)_3HCl$.

721. *Glycolylimide.*—On heating glycocine in a stream of hydrochloric acid gas, water is evolved, and neutral crystalline glycolylimide remains behind :



$$\begin{array}{lr} CH_2.(NH_3).O.CO & \\ | & | \\ CO.O.(NH_3).CH_2 & \end{array} = 2H_2O + \begin{array}{lr} CH_2.(NH).CO & \\ | & | \\ CO\ (NH)\ .\ CH_2 & \end{array} \text{ or } 2 \begin{array}{l} CH_2 \\ | \\ CO \end{array} \!\!> NH\ ?$$

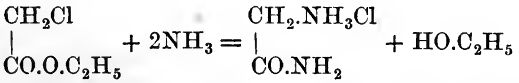
Glycolyl diamide is also known, and is formed by heating glycocine with alcoholic ammonia at 155° :



$$\begin{array}{lr} CH_2.(NH_3).O.CO & \\ | & | \\ CO.O.(NH_3).CH_2 & \end{array} + 2NH_3 = 2 \begin{array}{l} CH_2.NH_2 \\ | \\ CO.NH_2 \end{array} + 2H_2O$$

It is a colourless mass of strongly alkaline reaction, whose aqueous solution on evaporation partly decomposes into ammonia and glycocine.

Its hydrochloride is formed by heating ethylic chlor-acetate with alcoholic ammonia :



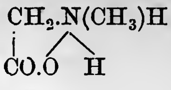
$$\begin{array}{l} CH_2Cl \\ | \\ CO.O.C_2H_5 \end{array} + 2NH_3 = \begin{array}{l} CH_2.NH_3Cl \\ | \\ CO.NH_2 \end{array} + HO.C_2H_5$$

in the form of readily soluble prisms, but the process also goes further and yields *diglycoloxyl diamidamine* hydrochloride :

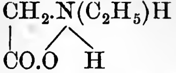
$$N(CH_2.CO.NH_2)_2H.HCl.$$

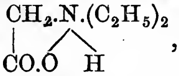
722. *Alkyl derivatives of glycocine* are obtained by the decomposition of chlor-acetic acid by excess of alkylamine bases. They behave like glycocine, yielding saline compounds with bases and mineral acids.

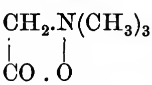
Methyl glycocine, or *sarcosine* :

$C_3H_7NO_2$ = 

is formed by long boiling of chlor-acetic acid with methylamine, and was obtained earlier as a product of the action of baric hydrate on caffeine and creatine. It crystallises in rhombic prisms of sweet taste, which are readily soluble in water, difficultly in alcohol, commence to sublime at 100°, and melt at a higher temperature.

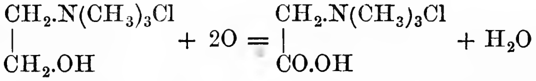
Ethyl glycocine, $C_4H_9NO_2$ =  , isomeric with ethylic amido-acetate, is prepared from chlor-acetic acid and ethylamine. It deliquesces in air and is also soluble in alcohol.

Diethyl glycocine, $C_6H_{13}NO_2$ =  , is obtained similarly from diethylamine.

Trimethyl glycocine, or *betaine*, 

$$\begin{array}{l} CH_2.N(CH_3)_3 \\ | \quad\quad | \\ CO\,.\,O \end{array}$$

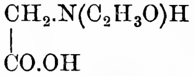
, occurs in the beet (*Beta vulgaris*), and is obtained as hydrochloride by boiling chloracetic acid with trimethylamine and by oxidation of choline hydrochloride:



$$\begin{array}{l} CH_2.N(CH_3)_3Cl \\ | \\ CH_2.OH \end{array} + 2O = \begin{array}{l} CH_2.N(CH_3)_3Cl \\ | \\ CO.OH \end{array} + H_2O$$

It is very soluble in water, deliquesces in air, and crystallises from nearly anhydrous alcohol in large brilliant crystals, containing one molecule H_2O, which they lose at 100°.

Probably the molecular formula of all the above alkyl glycocines should be doubled.

723. *Acetyl glycocine*, or *aceturic acid*, 

$$\begin{array}{l} CH_2.N(C_2H_3O)H \\ | \\ CO.OH \end{array}$$

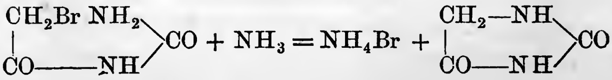
, corresponding to hippuric acid, is obtained from the silver compound of glycocine and acetylic chloride in the form of small white needles, readily soluble in water and alcohol. It is a monobasic acid, which decomposes carbonates.

Urea Derivatives of Glycocine.

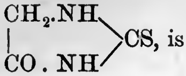
724. *Chlor-acetyl urea*, $CH_2.Cl.CO.NH.CO.NH_2$, and *brom-acetyl urea*, $CH_2Br.CO.NH.CO.NH_2$, are formed, similarly to acetyl-urea, by action of chlor-acetyl chloride and brom-acetyl bromide on urea. They crystallise in colourless needles, difficultly soluble in cold, decomposed by hot water.

On heating one of the preceding compounds with alcoholic ammonia, ammonic bromide is formed, together with

Glycolyl urea, or *hydantoïn*, $C_3H_4N_2O_2$:



in the form of colourless needles of sweet taste, difficultly soluble in cold water, melting at 206°, and resolidifying in crystals on cooling. Hydantoïn is also formed by heating hydriodic acid with allantoïn and alloxamic acid, and by boiling glycoluril with strong mineral acids.

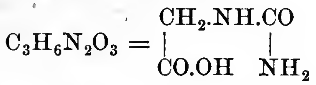


$$\begin{array}{l} CH_2.NH \\ | \qquad\quad \rangle CS \\ CO.NH \end{array}$$

Thio-hydantoïn, $\begin{array}{l} CH_2.NH \\ | \\ CO.NH \end{array}\rangle CS$, is obtained on gentle heating of thio-urea with chlor-acetic acid and precipitation of the solution by alkalies. It separates from water or alcohol in long thin needles.

On heating hydantoïn with solution of baric hydrate, it is converted into the baric salt of

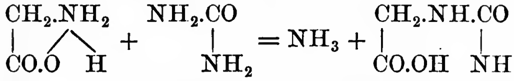
Hydantoïc acid, or glycoluramic acid :



$$C_3H_6N_2O_3 = \begin{array}{ll} CH_2.NH.CO & \\ | & \;\;| \\ CO.OH & NH_2 \end{array}$$

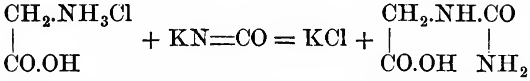
The free acid crystallises in colourless prisms of acid reaction, is soluble in water, but not in alcohol, and yields monobasic salts. The baric salt, $(NH_2.CO.NH.CH_2.CO.O)_2Ba$, is amorphous, most of its other salts crystalline.

It can be prepared by heating glycocine with urea :

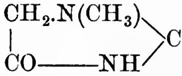


$$\begin{array}{l} CH_2.NH_2 \\ | \quad /\backslash \\ CO.O \quad H \end{array} + \begin{array}{c} NH_2.CO \\ | \\ NH_2 \end{array} = NH_3 + \begin{array}{ll} CH_2.NH.CO & \\ | & \;\;| \\ CO.OH & NH_2 \end{array}$$

and by the reaction of glycocine salts on potassic isocyanate :

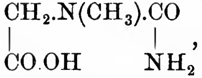


$$\begin{array}{l} CH_2.NH_3Cl \\ | \\ CO.OH \end{array} + KN{=}CO = KCl + \begin{array}{ll} CH_2.NH.CO & \\ | & \;\;| \\ CO.OH & NH_2 \end{array}$$



$$\begin{array}{l} CH_2.N(CH_3) \\ | \\ CO\text{———}NH \end{array}\rangle CO$$

725. *Methyl hydantoïn*, $C_4H_6N_2O_2 = \begin{array}{l} CH_2.N(CH_3) \\ | \\ CO\text{———}NH \end{array}\rangle CO$, is obtained by fusing together methyl glycocine with urea, as also by long heating of creatinine with solution of baric hydrate at 100°. It crystallises in colourless prisms, soluble in alcohol, melting at 156°-158°.



$$\begin{array}{ll} CH_2.N(CH_3).CO & \\ | & \quad | \\ CO.OH & NH_2 \end{array}$$

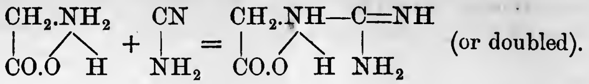
Methyl hydantoïc acid, $\begin{array}{ll} CH_2.N(CH_3).CO & \\ | & \quad | \\ CO.OH & NH_2 \end{array}$, can be obtained from sarcosine salts and potassic isocyanate; it crystallises in colourless tables; on heating in concentrated solution it loses water and yields methyl hydantoïn. It occurs in the organism after ingestion of sarcosine, then replacing urea in the urine.

Ethyl glycocine and urea yield at 120° *ethyl hydantoïn*, $C_6H_{10}N_2O_2$. It crystallises in tabular prisms, which melt at below 100°.

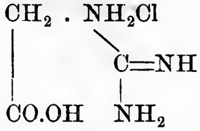
Guanidine Derivatives of Glycocine.

726. Guanidine derivatives of glycocine are obtained by the action of cyanamide on glycocine and its alkyl substitution products (comp. § 288), and occur in part naturally as important products of animal physiological processes.

Glycocyamine, $C_3H_7N_3O_2$, is formed directly when a solution of glycocine, cyanamide, and some ammonia is left to itself:



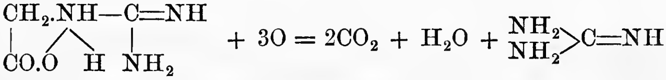
It soon separates in small colourless crystals, soluble in 126 parts of cold, more readily in hot, water, insoluble in alcohol and ether. It is dissolved readily by acids, forming with them salts probably similar to those of glycocine. The hydrochloride:



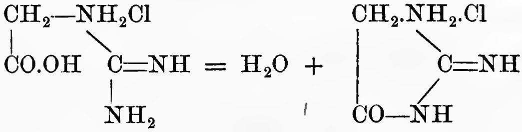
crystallises in large colourless prisms, and yields with platinic chloride yellowish red monoclinic prisms of the double salt:

$$(C_3H_7N_3O_2,HCl)_2PtCl_4,2H_2O.$$

Glycocyamine is readily oxidised to carbonic anhydride and guanidine by means of plumbic dioxide and dilute sulphuric acid:



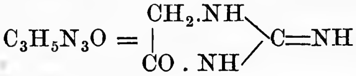
On heating glycocyamine hydrochloride to 160°, it melts, yields water, and becomes converted into *glycocyamidine hydrochloride*:



The latter yields, with platinic chloride, yellow needles of

$$(C_3H_5N_3O,HCl)_2PtCl_4,2H_2O;$$

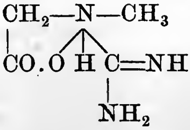
and by boiling with argentic oxide free *glycocyamidine*:



On evaporating the solution the latter separates in leafy crystals of alkaline reaction.

Glycocyamidine stands in the same relation to glycocyamine as hydantoïn to hydantoïc acid.

727. *Creatine*, $C_4H_9N_3O_2$, or *methyl glycocyamine*:



Creatine is a never-failing constituent of the flesh of all vertebrates, and can be obtained therefrom by extraction with cold water. It also occurs in smaller quantity in the urine and other parts of the animal organism. To prepare it the cold aqueous extract of flesh is freed from albumin by boiling, and phosphoric acid removed from the clear solution by addition of baric hydrate, the excess of the latter removed by passing carbonic anhydride into the liquid, which after filtration is evaporated to a syrup. On cooling, crystals of creatine separate, which increase on long standing. They are decolourised by treatment of their solution with animal charcoal. The granular concretions in commercial meat extract are due to creatine crystals.

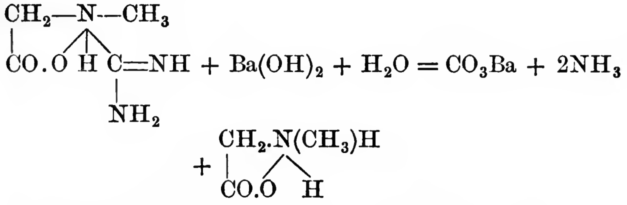
Creatine is obtained synthetically by the union of methyl glycocine or sarcosine (§ 722) with cyanamide.

Creatine crystallises in large, colourless, brilliant, short monoclinic prisms of the formula $C_4H_9N_3O_2,H_2O$, becoming cloudy at 100°, with loss of the water of crystallisation. It is soluble in 74 parts of cold, and in considerably less boiling, water. It is insoluble in absolute alcohol and ether.

With the mineral acids creatine yields salts of acid reaction corresponding to those of glycocyamine, whose solutions can only be brought to unchanged crystallisation at ordinary temperatures, being converted on heating into salts of creatinine.

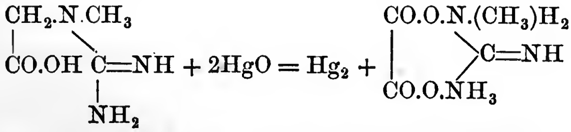
Creatine nitrate, $C_4H_9N_3O_2,HNO_3$, crystallises in large colourless prisms.

On boiling with solution of baric hydrate, creatine is decomposed into sarcosine, carbonic acid, and ammonia :



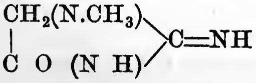
$$\begin{array}{l} CH_2{-}N{-}CH_3 \\ \;| \\ CO.O\;H\;C{=}NH + Ba(OH)_2 + H_2O = CO_3Ba + 2NH_3 \\ \qquad\quad\;\; | \\ \qquad\quad NH_2 \\ \qquad\qquad\qquad\qquad\quad CH_2.N(CH_3)H \\ \qquad\qquad\qquad\qquad + \;| \\ \qquad\qquad\qquad\qquad\quad CO.O\;\;H \end{array}$$

It is oxidised by plumbic peroxide and sulphuric acid to methyl guanidine (methyl uramine, § 288), carbonic anhydride, and water. If mercuric oxide be employed as the oxidising agent, methyl guanidine oxalate is formed :



$$\begin{array}{l} CH_2.N.CH_3 \\ \;| \\ CO.OH\;C{=}NH + 2HgO = Hg_2 + \\ \qquad\quad\;\; | \\ \qquad\quad NH_2 \end{array} \begin{array}{l} CO.O.N.(CH_3)H_2 \\ \;|\qquad\qquad\qquad \rangle C{=}NH \\ CO.O.NH_3 \end{array}$$

728. *Creatinine*, $C_4H_7N_3O$, or *methyl glycocyamidine :*



$$\begin{array}{l} CH_2(N.CH_3) \\ \;| \qquad\qquad\qquad \rangle C{=}NH \\ C\;\;O\;\;(N\;\;H) \end{array}$$

is readily formed from creatine, with removal of water, by heating with dilute mineral acids ; e.g. on evaporating a solution of creatine sulphate on the water bath, creatinine sulphate is left, from which, by treatment with baric carbonate, the sulphuric acid is removed and free creatinine obtained by evaporation of the filtrate.

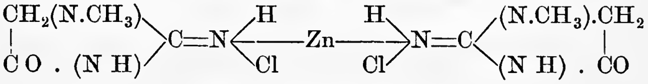
Creatinine does not occur in flesh, but does in urine, a fully grown man excreting about ·6 – 1·3 gram creatinine in 24 hours. In order to prepare it from urine, this is concentrated to about $\frac{1}{8}$ of its bulk, then made faintly alkaline by means of milk of lime, and calcic chloride added so long as a precipitate—consisting mainly of calcic phosphate—falls down. The filtrate is evaporated to a syrup, the sodic chloride which crystallises out removed, and the mother liquor mixed with a syrupy solution of zincic chloride. The difficultly soluble creatinine zincic chloride soon separates, which is purified by crystallisation and decomposed by boiling with water and plumbic oxide. Basic plumbic chloride and zincic oxide precipitate whilst the solution contains creatinine and creatine—formed from the former by union with water—which, after evaporation to dryness, are separated by means of alcohol.

Creatinine crystallises in long colourless monoclinic prisms, which dissolve readily in water and alcohol, and have a strongly alkaline reaction. It unites with acids to form salts of neutral reaction, which contain an equivalent of acid to each molecule of creatinine. The hydrochloride yields with platinic chloride a double salt:

$$(C_4H_7N_3O,HCl)_2,PtCl_4,$$

pretty soluble in water, difficultly in alcohol.

A very characteristic creatinine salt is *creatinine zincic chloride*, $(C_4H_7N_3O)_2ZnCl_2$. In this hydrogen has been replaced by zinc somewhat in the fashion of the formula:

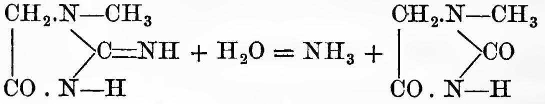


It crystallises in groups of fine needles, difficultly soluble in water, insoluble in alcohol.

With hydrochloric acid it yields a further very readily soluble crystalline salt, $(C_4H_7N_3O.HCl)_2ZnCl_2$.

By long contact with water creatinine is converted into creatine, especially in the presence of basic hydrates, so that it can only be obtained in part unaltered from its salts.

By boiling with solution of baric hydrate, ammonia is first evolved, methyl hydantoïn being formed (§ 725):



which soon decomposes into methyl glycocine, baric carbonate, and ammonia. With mercuric oxide or plumbic dioxide and sulphuric acid it yields the same products as creatine.

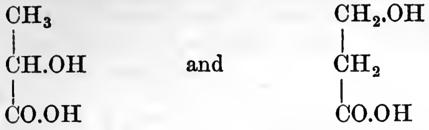
On heating creatinine for a long time at 100° with alcohol and ethylic iodide, *ethyl creatinine hydriodide*, $C_4H_6(C_2H_5)N_3O,HI$, is formed, from which argentic oxide liberates *ethyl creatine*:

$$C_4H_8(C_2H_5)N_3O_2,$$

crystallising in needles grouped in bundles, of strongly alkaline reaction.

Lactic Acids, $C_3H_6O_3$.

729. The isomeric lactic acids occupy the second place in the series of hydroxy acids. So far as these are hydroxy-propionic acids there can only be two isomers, namely:



$$\begin{array}{c} CH_3 \\ | \\ CH.OH \\ | \\ CO.OH \end{array} \qquad \text{and} \qquad \begin{array}{c} CH_2.OH \\ | \\ CH_2 \\ | \\ CO.OH \end{array}$$

α-Hydroxy-propionic acid, or ethylidene hydrate carbonic acid.

β-Hydroxy-propionic acid, or ethylene hydrate carbonic acid.

There are, however, four isomeric monobasic acids known of this formula, $C_3H_6O_3$, of which two, *ordinary lactic* and *paralactic acids*, have the structural formula of α-hydroxy-propionic acid; *ethylene lactic acid* is β-hydroxy-propionic acid, whilst in the case of the fourth, *hydracrylic acid*, the order of arrangement of the atoms has not yet been determined with certainty.

1. *Ordinary or Fermentation Lactic Acid.*

Optically Inactive Ethylidene Lactic Acid, $CH_3.CH(OH).CO.OH$.

730. Ordinary lactic acid occurs in small quantity in the animal organism, especially in the gastric juice, and is formed under certain circumstances in the fermentation of some sugars. In the latter way it is formed in sour milk, in sauerkraut, &c.

It is prepared from propionic acid by means of the halogen substitution products. On heating dry propionic acid with a molecule of bromine in closed tubes to 130°, the liquid soon decolourises, and then contains, together with much hydrobromic acid, principally α-brompropionic acid:

$$CH_3.CH_2.CO.OH + Br_2 = CH_3.CHBr.CO.OH + HBr.$$

The salts of this latter, on boiling with water, alkalies, or argentic oxides, are converted into α-oxypropionic acid, just as the haloid acetic acids are converted into glycollic acid:

$$CH_3.CHBr.CO.OAg + H_2O = AgBr + CH_3.CH(OH).CO.OH.$$

Its structure is shown by its synthetical preparation from ethylidene compounds, especially from ethylidene oxide or acetic aldehyde (§ 390). On mixing the latter with hydrocyanic acid, they unite together to form *ethylidene hydrate cyanide*, which on treatment with strong hydrochloric acid is converted into lactic acid even at the ordinary temperature. Aldehyde ammonia is converted by prussic acid into ethylidene-amide cyanide, this by aqueous hydrochloric acid into alanine, and the latter is converted into lactic acid by nitrous acid (formulæ and equations, § 705, 5, *a* and *b*).

Other methods of formation of ordinary lactic acid, as from glyceric acid and pyrotartaric acid, will be mentioned later at their respective places.

Lactic acid is most readily prepared by a peculiar fermentation of sugar. For this purpose 3 kilograms of cane sugar and 15 grams of tartaric acid are dissolved in 17 litres of boiling water. Thereby the cane sugar, $C_{12}H_{22}O_{11}$, is split up under the influence of the tartaric acid, and with combination with a molecule of water, into $2C_6H_{12}O_6$ (grape sugar and fruit sugar). There is then added, to sow the necessary ferment, 100 grams of old cheese or of putrid flesh, mixed with 4 litres of sour milk, and 1½ kilogram of zinc white or zinc carbonate, and the whole allowed to stand for a long time, best at a temperature of 40°–45°. After eight to ten days the change :

$$C_6H_{12}O_6 = 2C_3H_6O_3,$$

is finished, and at the bottom of the vessel, in place of the basic zinc salt, crusts of zincic lactate are found, which are purified by recrystallisation from hot water and then decomposed in boiling solution by sulphuretted hydrogen. The liquid, freed from zincic sulphide, is then evaporated to a thin syrup on the water bath, and separated from any undecomposed zinc salt or mannite by solution in ether. The separated ethereal solution is distilled from the water bath, and finally warmed for some time in an open vessel.

In this way there is obtained a colourless, strongly acid syrup, from which, however, pure lactic acid of the formula $C_3H_6O_3$ cannot be obtained. If much water is present there is no doubt a body of the formula :

$$CH_3.CH(OH).C(OH)_3,$$

which, on further evaporation, decomposes into water and lactic acid. As soon as the latter has attained certain proportions, single lactic acid molecules etherify, and both ethereal anhydrides are formed in greater proportion the further the concentration is carried. The syrupy preparation termed lactic acid is therefore a mixture of $CH_3.CH(OH).C(OH)_3$, $CH_3.CH(OH)CO.OH$, $C_6H_{10}O_5$, and often also of $C_6H_8O_4$. On further drying in vacuo over sulphuric acid it becomes quite stiff, and then consists essentially of the two ethereal anhydrides.

By distillation of an aqueous solution much unaltered lactic acid passes over in the aqueous vapour ; by heating the syrupy preparation, on the other hand, the formation of the ethereal anhydrides is increased. If the temperature is raised slowly, much of the second anhydride (lactide) volatilises, whilst by quick heating to higher temperatures the greater part is decomposed into aldehyde, carbonic oxide, and water :

$$CH_3.CH(OH).CO.OH = CH_3.CHO + CO + H_2O.$$

By heating with dilute sulphuric acid to 130° it is decomposed into aldehyde and formic acid :

$$CH_3.CH(OH).CO.OH = CH_3.CHO + HCO.OH.$$

Oxidising agents, e.g. chromic acid, oxidise it to acetic acid, carbonic anhydride, and water :

$$CH_3.CH(OH).CO.OH + 2O = CH_3.CO.OH + CO_2 + OH_2.$$

By heating with concentrated hydriodic acid, lactic acid is reduced to propionic acid (α-iodo-propionic acid being first formed) :

$$CH_3.CH(OH).CO.OH + 2HI = H_2O + I_2 + CH_3.CH_2.CO.OH.$$

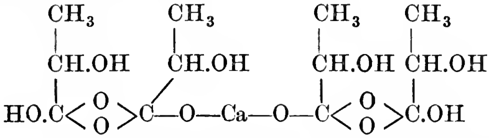
Putrefactive ferments convert a solution of lactic acid or its salts into normal butyric acid.

731. *Lactates.*—In the replacement of hydroxylic hydrogen by metals, lactic acid acts as a monobasic acid, which is also a monhydric alcohol. Carbonates only replace the acid hydrogen, as do also most of the basic hydrates; the alkaline salts, on heating with alkali metal, have their alcohol-hydroxylic hydrogen atom replaced also.

The neutral alkali salts of lactic acid are deliquescent, also soluble in alcohol, and yield on evaporation of their solutions solid amorphous masses, which melt on gentle heating.

Sodic lactate, $CH_3.CH(OH).CO.ONa$, after long drying in vacuo forms a solid mass, consisting of fine hair-like crystals. When fused it dissolves sodium with evolution of hydrogen, and is converted partially into the compound $CH_3.CH(ONa)CO.ONa$, which, like the sodic alkylates, is decomposed by water into free alkali and neutral salt.

Calcic lactate, $[CH_3.CH(OH).CO.O]_2Ca,5H_2O$, crystallises in aggregates of small thin needles, soluble in 9½ parts of cold water and also in alcohol. If the aqueous solution is mixed with two molecules of lactic acid, an *acid* salt, $C_6H_{10}CaO_6,2C_3H_6O_3,2H_2O_2$, crystallises on evaporation. This may be expressed by a formula similar to that given for the acid acetates:

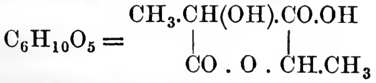


The double salt, $C_6H_{10}CaO_6,2C_3H_5KO_3$, obtained by evaporation of equivalent quantities of the calcic and potassic salts, has a similar constitution.

Zincic lactate, $C_6H_{10}ZnO_6,3H_2O$, is the most characteristic salt of lactic acid. It crystallises in small colourless monoclinic prisms, generally united to crusts. It requires for solution about sixty parts of cold, and only six parts of boiling, water. It is nearly insoluble in alcohol. Ferrous lactate, $[CH_3.CH(OH)CO.O]_2Fe,3H_2O$, possesses similar properties.

732. *Ethereal Anhydrides of Lactic Acid.*—As already mentioned, the ethereal anhydrides are obtained from lactic acid in a dry atmosphere even at ordinary temperatures, as also on heating, especially at temperatures above 100°.

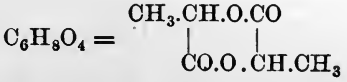
First ethereal anhydride, lactyl lactate:



$$C_6H_{10}O_5 = \begin{array}{l} CH_3.CH(OH).CO.OH \\ \qquad\ \ | \qquad\quad\ \ | \\ \qquad CO\ .\ O\ .\ CH.CH_3 \end{array}$$

is a yellow amorphous mass, scarcely soluble in water, but readily in alcohol and ether; on boiling with water or alkalies it is reconverted into lactic acid.

The dehydration easily proceeds further, yielding the *second ethereal anhydride,* or *lactide:*



$$C_6H_8O_4 = \begin{array}{l} CH_3.CH.O.CO \\ \qquad | \qquad\ \ | \\ \qquad CO.O.CH.CH_3 \end{array}$$

This is obtained in larger quantity when lactic acid or the first ethereal anhydride is heated for a long time at 150° in a tubulated retort through which a slow stream of air is drawn. The neck of the retort is soon coated with a crystalline coating of lactide, which is from time to time removed by fusion, washed with cold alcohol, and finally crystallised from boiling alcohol.

Lactide forms colourless rhombic tables, melting at 124·5° and distilling at 255°. The vapour density is 4·81. It is insoluble in water, but is slowly decomposed thereby into the first ethereal anhydride, and finally into lactic acid. It is much more readily saponified by alkalies.

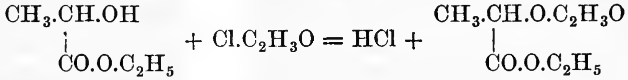
733. *Ethylic lactate*, $CH_3.CH(OH).CO.O.C_2H_5$, is formed by heating lactic acid, or still better a mixture of the anhydrides, with alcohol to 170°. Ethylic lactate is separated from the products by fractional distillation as a colourless liquid of peculiar odour, boiling at 156°, which mixes with water, but is soon decomposed by this into alcohol and acid.

Sodium dissolves in pure ethylic lactate with evolution of hydrogen, as in an alcohol, yielding the so-called *ethylic sodio-lactate :*

$$CH_3.CH(ONa)CO.O.C_2H_5,$$

a solid mass decomposed by water into free alkali and ethylic lactate which then further react on each other as above.

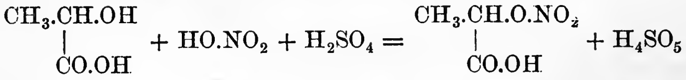
734. On mixing ethylic lactate with an acid haloid, e.g. with acetyl chloride, the alcoholic group of the former reacts energetically with the halogen compound (§ 608), *ethylic aceto-lactate* being formed :



$$\begin{array}{c} CH_3.CH.OH \\ | \\ CO.O.C_2H_5 \end{array} + Cl.C_2H_3O = HCl + \begin{array}{c} CH_3.CH.O.C_2H_3O \\ | \\ CO.O.C_2H_5 \end{array}$$

It boils at 177°, has an agreeable odour, sp. gr. 1·0458 at 17°, and is insoluble in water. If heated with a little water to 150°, and then submitted to distillation, ethylic alcohol passes over, whilst a strongly acid syrup of *aceto-lactic acid*, $CH_3.CH(O.C_2H_3O)CO.OH$, remains behind. This yields in general gummy salts, completely decomposed on long heating, or more readily by boiling with alkalies, into lactic and acetic acids or the respective salts.

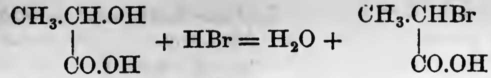
735. *Nitro-lactic acid*, or *lactic acid nitrate*, is prepared by introducing syrupy lactic acid into a mixture of concentrated sulphuric and nitric acids :



$$\begin{array}{c} CH_3.CH.OH \\ | \\ CO.OH \end{array} + HO.NO_2 + H_2SO_4 = \begin{array}{c} CH_3.CH.O.NO_2 \\ | \\ CO.OH \end{array} + H_4SO_5$$

and is extracted from the reaction mass after dilution with water by shaking with ether. It forms a thick, strongly acid liquid but little soluble in water, readily soluble in alcohol and ether, and decomposes on standing.

736. *Halogen Compounds of Lactyl.*—On saturating lactic acid with hydrochloric or hydrobromic acid and heating in sealed glass tubes, *α-halogen propionic acids* are formed :

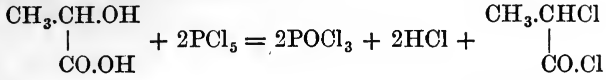


$$\begin{array}{l}CH_3.CH.OH\\ \quad\;\;|\\ \quad\;\;CO.OH\end{array} + HBr = H_2O + \begin{array}{l}CH_3.CHBr\\ \quad\;\;|\\ \quad\;\;CO.OH\end{array}$$

The same compound is formed, as already mentioned, by the action of chlorine or bromine on propionic acid, and can be reconverted into propionic acid by treatment of their aqueous solutions with sodium amalgam :

$$CH_3.CHCl.CO.OH + Na_2 = NaCl + CH_3.CH_2.CO.ONa.$$

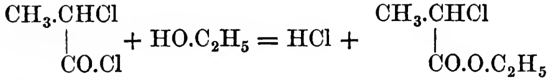
On mixing lactic acid or a lactate with phosphorus haloids, double haloids are formed :



$$\begin{array}{l}CH_3.CH.OH\\ \quad\;\;|\\ \quad\;\;CO.OH\end{array} + 2PCl_5 = 2POCl_3 + 2HCl + \begin{array}{l}CH_3.CHCl\\ \quad\;\;|\\ \quad\;\;CO.Cl\end{array}$$

α-Chlor-propionic chloride.

The latter, on treatment with water and alcohols, only suffer decomposition in the carboxyl haloid group, so that α-halogen propionic acids or their salts are formed :



$$\begin{array}{l}CH_3.CHCl\\ \quad\;\;|\\ \quad\;\;CO.Cl\end{array} + HO.C_2H_5 = HCl + \begin{array}{l}CH_3.CHCl\\ \quad\;\;|\\ \quad\;\;CO.O.C_2H_5\end{array}$$

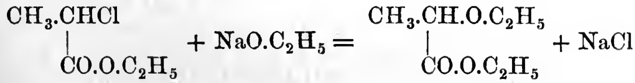
α-Chlor-propionic acid, $C_3H_5ClO_2{=}CH_3.CHCl.CO.OH$, is a colourless liquid of strongly acid reaction, of sp. gr. 1·28, boiling at 186°, whose salts on long boiling with water decompose into metallic chlorides and lactic acid. Its ethylic salt, $CH_3.CHCl.CO.O.C_2H_5$, boils at 144°. *α-Chlor-propionic chloride*, also termed lactyl dichloride, is best prepared from dry calcic lactate and phosphoric pentachloride. It is a liquid fuming in air, always somewhat decomposed on distillation, and cannot be separated completely from phosphoric oxychloride.

α-Brom-propionic acid, $CH_3.CHBr.CO.OH$, boils at 202°–205°, and solidifies in crystals at − 17°. Its ethylic salt decomposes somewhat on distillation.

α-Iod-propionic acid, $CH_3.CHI.CO.OH$, is a thick brown oil scarcely soluble in water.

737. *Ether Derivatives of Lactic Acid.*—Compounds in which the alcoholic hydroxylic hydrogen in lactic acid is replaced by alcohol radicals can be prepared in different ways. Either ethylic chlor or brom propionate is heated with sodic alkylates, or ethylic sodic lactate is treated with alkyl iodides.

Ethylic ethyl-lactate, $CH_3.CH(O.C_2H_5).CO.O.C_2H_5$, is most readily prepared according to the equation :



$$\begin{array}{l}CH_3.CHCl\\ \quad\;\;|\\ \quad\;\;CO.O.C_2H_5\end{array} + NaO.C_2H_5 = \begin{array}{l}CH_3.CH.O.C_2H_5\\ \quad\;\;|\\ \quad\;\;CO.O.C_2H_5\end{array} + NaCl$$

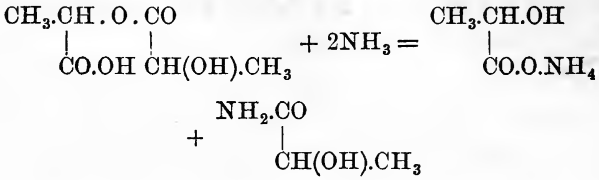
It is a colourless liquid, boiling at 156·5°, soluble in water, saponified by alkalies into the salts of

Ethyl-lactic acid, $CH_3.CH(O.C_2H_5)CO.OH$. This latter is a strongly acid, distillable liquid, isomeric with ethylic lactate.

738. *Amide Derivatives of Lactyl.*—Lactic acid, like glycollic acid, yields two isomeric amides, one from the acid group and one, corresponding to glycocine, from the alcohol group of the molecule.

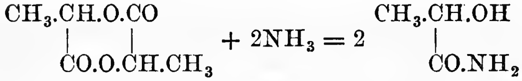
Lactamide, $CH_3.CH(OH).CO.NH_2$, is formed from all the ethereal salts of lactic acid by the action of ammonia in alcoholic or aqueous solution :

$$CH_3.CH(OH).CO.O.C_2H_5 + NH_3 = HO.C_2H_5 + CH_3.CH(OH).CO.NH_2,$$



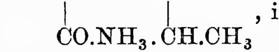
$$\begin{array}{l}CH_3.CH.O.CO\\ \quad | \qquad\ |\\ CO.OH\ CH(OH).CH_3\end{array} + 2NH_3 = \begin{array}{l}CH_3.CH.OH\\ \quad |\\ CO.O.NH_4\end{array} + \begin{array}{l}NH_2.CO\\ \quad |\\ CH(OH).CH_3\end{array}$$

and

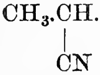


$$\begin{array}{l}CH_3.CH.O.CO\\ \quad | \qquad |\\ CO.O.CH.CH_3\end{array} + 2NH_3 = 2\ \begin{array}{l}CH_3.CH.OH\\ \quad |\\ CO.NH_2\end{array}$$

It crystallises in colourless leafy crystals, melting at 74° and dissolving readily in water, alcohol, and ether. On heating with water it yields ammonic lactate; by boiling with alkalies, alkaline lactates and free ammonia.



Alanine, or amido-propionic acid, $CH_3.CH(NH_2).CO.OH$, or more probably $\begin{array}{l}CH_3.CH.NH_3.CO\\ \quad | \qquad\quad |\\ CO.NH_3.CH.CH_3\end{array}$, is obtained from α-chlor-propionic acid and ammonia, or more readily from aldehyde ammonia. This is dissolved in excess of aqueous hydrocyanic and boiled for a long time with dilute hydrochloric acid. Ethylidene amide cyanide,

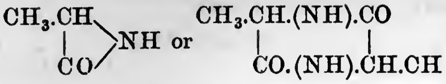


$\begin{array}{l}CH_3.CH.NH_2\\ \quad |\\ \quad CN\end{array}$, first formed, is thereby decomposed into ammonic chloride and alanine hydrochloride. The solution is evaporated to dryness, and the latter salt dissolved in alcohol. To prepare alanine from this, its aqueous solution is boiled with plumbic hydrate, filtered from basic plumbic chloride, excess of lead removed by sulphuretted hydrogen, and the clear filtrate evaporated.

Alanine crystallises in brilliant rhombic prisms of neutral reaction and sweet taste. Water dissolves it readily, alcohol difficultly, and it is insoluble in ether. By careful heating it can be sublimed in part unchanged, but readily decomposes into equal molecules of carbonic anhydride and ethylamine. It behaves towards acids, alkalies, salts, and oxides of the heavy metals in like manner to glycocine. The acid salts, e.g. $CH_3.CH(NH_3Cl).CO.OH$, dissolve in alcohol, react strongly acid, and generally crystallise well. By nitrous acid it is oxidised to lactic acid.

On heating alanine in a stream of hydrochloric acid gas it loses water and is converted into

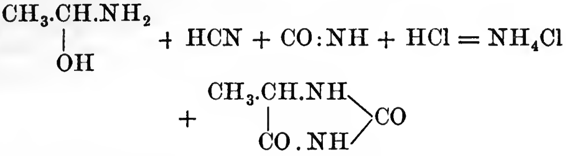
Lactimide, or *lactoxylimide* :



$$\begin{array}{l} CH_3.CH \\ \quad | \qquad > NH \\ \quad CO \end{array} \text{ or } \begin{array}{l} CH_3.CH.(NH).CO \\ \quad | \qquad\qquad\qquad | \\ \quad CO.(NH).CH.CH \end{array}$$

crystallising in colourless needles or leaves, melting at 275°, and dissolving readily in water and alcohol.

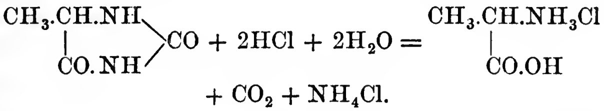
739. *Lactoxyl Urea.*—If a mixture of aldehyde ammonia, potassic cyanide, and potassic pseudo-cyanate be slowly decomposed with hydrochloric acid, and the brown reaction product extracted with ether alcohol, there is found in solution *lactyl urea*, isomeric with methyl hydantoïn (§ 724). It forms transparent rhombic prisms of the formula $C_4H_6N_2O_2,2H_2O$; when anhydrous it melts at 145° :



$$\begin{array}{l} CH_3.CH.NH_2 \\ \quad | \\ \quad OH \end{array} + HCN + CO{:}NH + HCl = NH_4Cl$$

$$+ \begin{array}{l} CH_3.CH.NH \\ \quad | \qquad\qquad > CO \\ \quad CO.NH \end{array}$$

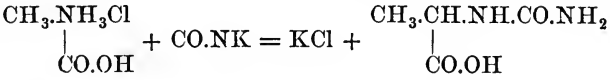
On heating with hydrochloric acid it splits up into alanine hydrochloride, ammonic chloride, and carbonic anhydride :



$$\begin{array}{l} CH_3.CH.NH \\ \quad | \qquad\qquad > CO \\ \quad CO.NH \end{array} + 2HCl + 2H_2O = \begin{array}{l} CH_3.CH.NH_3Cl \\ \quad | \\ \quad CO.OH \end{array}$$

$$+ CO_2 + NH_4Cl.$$

Alanine salts, when treated with potassic isocyanate, yield *lacturaminic acid*, $C_4H_8N_3O_3$, homologous with hydantoïc acid :

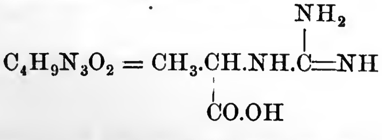


$$\begin{array}{l} CH_3.NH_3Cl \\ \quad | \\ \quad CO.OH \end{array} + CO.NK = KCl + \begin{array}{l} CH_3.CH.NH.CO.NH_2 \\ \quad | \\ \quad CO.OH \end{array}$$

Its amorphous baric salt is also prepared by heating lactyl urea with baric hydrate.

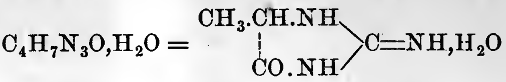
Lacturaminic acid crystallises in small rhombic prisms of melting point 155° ; it yields salts, which in great part crystallise well, e.g. $CH_3.CH(NH.CO.NH_2)CO.OAg$, and is also decomposed by hydrochloric acid into alanine hydrochloride, ammonic chloride, and carbonic anhydride.

740. *Lactyl guanidine*, or *alacreatine* :



$$C_4H_9N_3O_2 = \begin{array}{l} \qquad\qquad\qquad\quad NH_2 \\ \qquad\qquad\qquad\quad | \\ CH_3.CH.NH.C{=}NH \\ \quad | \\ \quad CO.OH \end{array}$$

isomeric with creatine, is formed from alanine and cyanamide, and crystallises in small prisms, requiring twelve times their weight of water at 15° for solution. It comports itself quite similarly to glycocyamine and creatine; e.g. on heating its salts are converted with loss of water into salts of *alacreatinine.* This latter crystallises in long prisms of alkaline reaction and of the formula



$$C_4H_7N_3O,H_2O = \begin{array}{l} CH_3.CH.NH \\ \quad | \\ CO.NH \end{array} \!\!> C{=}NH,H_2O$$

and, like creatinine and glycocyamidine, forms a difficultly soluble compound with zincic chloride.

741. *Nitriles.*—By direct union of acetic aldehyde with hydrocyanic acid there is formed *ethylidene hydrate cyanide,* or *lactyl hydrate nitrile,* $CH_3CH(OH).CN$, a colourless liquid mixing in every proportion with water and alcohol. It boils at 183° with partial decomposition into its components, and in presence of aqueous mineral acids is transformed into ammonic salts and lactic acid.

The *nitrile* of *ethyl-ether lactic acid,* $CH_3.CH(O.C_2H_5).CN$, is obtained by distillation of its amide with phosphoric anhydride (comp. § 545) as a clear mobile liquid boiling at 134°–135°, whose sp. gr. at 6° = ·918.

2. *Paralactic or Optically Active Ethylidene Lactic Acid.*

742. Paralactic acid occurs, together with ethylene lactic acid, in the juice of flesh, and is especially formed in large quantity during muscular exertion and after *rigor mortis* has set in. It can be obtained from the mother liquor from which creatine has been crystallised (§ 727) by acidulation and repeated shaking with ether, in which it is soluble. The ethereal solution is separated, distilled, and the strongly acid residue, after addition of water, treated with plumbic carbonate. The filtered liquid is then treated with hydric sulphide to remove lead, saturated whilst boiling with zincic carbonate, and the liquid evaporated till crystallisation commences. Four to five times the volume of strong alcohol is then added, when zincic paralactate separates as a crystalline mud, which is purified by repeated solution in water and precipitation with alcohol, and finally by recrystallisation from hot water. The alcoholic filtrate always contains some zincic ethylene lactate in addition to the paralactate.

To prepare it from commercial flesh extract, the latter is dissolved in four times its weight of luke-warm water, and then mixed with double the volume of 90 % alcohol. The brown precipitate consists mainly of inorganic salts and creatine. The alcoholic liquid contains, together with other bodies, the salts of paralactic acid ; it is evaporated to a syrup, and once more extracted with several times its volume of alcohol. The syrupy residue left on evaporating this last extract is acidulated with dilute sulphuric acid, and the liberated lactic acids extracted with ether and purified as above.

The free acid is prepared as a syrup by treatment of a warm concentrated solution of the zinc salt with hydric sulphide and evaporation of the filtrate.

Paralactic acid completely resembles fermentation lactic acid, except that its aqueous solution rotates the plane of polarisation slightly to the *right.* By long standing in a dry atmosphere at ordinary temperatures it is converted, like fermentation lactic acid, into ethereal anhydrides, which, however, rotate the plane of a polarised beam of light strongly to the left (a mixture of 84 % of the first anhydride and 16 % lactide in a tube ·1 metre long = − 85·9°).

If the ethereal anhydrides be prepared by *heating*, they are then obtained optically inactive, and on saponification by water or alkalies yield ordinary fermentation lactic acid.

On heating paralactic acid with dilute sulphuric acid to 130°–150° it is resolved into formic acid and acetic aldehyde; if chromic acid be also employed, acetic acid is formed from the latter. These are the same products as are afforded by fermentation lactic acid, and therefore the two acids must have an identical structure, i.e. the elementary atoms must be united together in the same order. Fermentation and para lactic acids can therefore only be regarded as physically isomeric compounds (comp. § 47).

The *salts* of paralactic acid resemble those of fermentation lactic acid, but are distinguished therefrom by differences in the amount of water of crystallisation and somewhat different solubilities. These differences are especially noticeable in the zinc salts. *Zincic paralactate* contains only two molecules of water of crystallisation:

$$(C_3H_5O_3)_2Zn,2H_2O,$$

and on slow evaporation crystallises in *single* short and thick but small prisms. It is scarcely soluble in alcohol, dissolves in 18·5 parts of water at 14°–15°, and readily yields supersaturated solutions, which only arrive slowly at their normal concentration. Its solution—as those of all other paralactates—rotates the plane of polarisation to the *left*.

Further derivatives of paralactic acid have not yet been prepared.

3. *Ethylene Lactic Acid.*

743. Ethylene lactic acid can be prepared synthetically from its nitrile. This, *ethylene hydrate cyanide*, is obtained by heating ethylene hydrate chloride with an alcoholic solution of potassic cyanide:

$$HO.CH_2.CH_2.Cl + KCN = HO.CH_2.CH_2.CN + KCl.$$

After evaporation of the solution filtered from the potassic chloride the residue is extracted with a mixture of equal volumes of absolute alcohol and ether, which dissolves the nitrile and leaves it on evaporation as a yellowish syrup. On boiling with alkalies it is converted with evolution of ammonia into potassic ethylene lactate:

$$HO.CH_2.CH_2.CN + H_2O + HOK = NH_3$$
$$+ HO.CH_2.CH_2.CO.OK.$$

This salt is decomposed by an excess of dilute sulphuric acid, and the free acid extracted with ether. It contains as a rule a slight admixture of fermentation lactic acid, from which it can be purified, though with difficulty, by conversion into the zinc salt, &c.

The same acid apparently occurs, together with paralactic acid, in extract of meat, and is found in the alcoholic solution filtered from the zincic paralactate; this yields on evaporation a syrup in which numerous crystals of zincic paralactate are embedded. Its preparation in a state of approximate purity is attended with great difficulties, and can only be effected by repeated treatment with very strong alcohol and final precipitation of a part of the salt with ether, until the zinc salt remaining dissolved is obtained completely amorphous on evaporation. The free acid is then liberated by hydric sulphide.

Ethylene lactic acid forms a syrup, closely resembling ethylidene lactic acid. Its alkali salts are very soluble; the sodic salt yields, on complete evaporation on the water bath, a solid crystalline mass, soluble in alcohol and crystallising from the boiling alcoholic solution in indistinct forms.

Zincic ethylene lactate is completely amorphous; it is somewhat decomposed at 100°, becoming yellow-coloured, so that it can only be completely dried in vacuo. It gives at first a transparent gummy mass, which becomes turbid on complete drying. Its composition is then $(C_3H_5O_3)_2Zn$.

By oxidation with nitric acid or with chromic and sulphuric acids it yields no acetic acid, but carbonic anhydride and oxalic acids. A mixture of paralactic and ethylene lactic acids, such as is obtained from extract of meat, on the other hand, yields malonic acid, which can only be formed from the ethylene lactic acid:

$$HO.CH_2.CH_2.CO.OH + 2O = H_2O + \underset{\text{(Malonic acid.)}}{HO.CO.CH_2.CO.OH}.$$

By heating with hydriodic acid it does not yield crystalline iodo-propionic acid.

4. *Hydracrylic Acid.*

744. If glyceric acid, obtained by the oxidation of glycerine, be heated in syrupy solution with phosphorus iodide, a violent reaction occurs with evolution of hydriodic acid, and on cooling the mass solidifies to a crystalline pulp of *β-iodo-propionic acid:*

$$C_3H_6O_4 + 3HI = I_2 + 2H_2O + C_3H_5IO_2.$$

The same body is obtained by heating acrylic acid and a solution of hydriodic acid at 120°:

$$C_3H_4O_2 + HI = C_3H_5IO_2.$$

It crystallises in large, colourless, brilliant plates, which melt at 82° and are difficultly soluble in cold, readily in hot, water. By heating with concentrated hydriodic acid to at least 180° it is converted into propionic acid.

By treatment with chlorine water iodine is eliminated and *β-chlor-propionic acid* formed:

$$2C_3H_5IO_2 + Cl_2 = I_2 + 2C_3H_5ClO_2,$$

which forms leafy crystals melting at 40·5°, and which can also be prepared by combining acrylic and hydrochloric acids.

β-Brom-propionic acid can be prepared in exactly analogous manner to the last; it forms crystals melting at 61·5°.

745. On adding freshly precipitated argentic oxide to a hot solution of β-iodo-propionic acid, as long as argentic iodide separates, *hydracrylic acid* is formed:

$$C_3H_5IO_2 + AgOH = AgI + C_3H_5(OH)O_2.$$

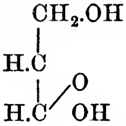
The liquid is treated with sulphuretted hydrogen to remove excess of silver, and the filtrate saturated when hot with zincic carbonate. By slow evaporation zincic hydracrylate is obtained in beautiful prisms, from which pure hydracrylic acid can be separated by hydric sulphide.

Hydracrylic acid is syrupy, like the other lactic acids, does not yield ethereal anhydrides on heating or acetic aldehyde on dry distillation, but is converted into water and acrylic acid :

$$C_3H_6O_3 = H_2O + C_3H_4O_2.$$

By careful oxidation with chromic acid or nitric acid it is converted into carbonic anhydride and glycollic acid, the latter being readily further oxidised to oxalic acid.

The constitution of hydracrylic acid is not yet sufficiently clear, but the results of oxidation and other considerations render probable the formula :



By heating with hydriodic acid it is readily reconverted into β-iodo-propionic acid :

$$C_3H_6O_3 + HI = H_2O + C_3H_5IO_2.$$

The salts of hydracrylic acid differ very essentially from those of all the isomeric acids.

The *sodic salt* separates from boiling nearly absolute alcohol in colourless anhydrous crystals of the formula $C_3H_5O_3Na$, melting at 143°.

Calcic hydracrylate, $(C_3H_5O_3)_2Ca,2H_2O$, crystallises in rhombic prisms, which readily part with their water of crystallisation.

Zincic hydracrylate, $(C_3H_5O_3)_2Zn,4H_2O$, crystallises in large well-formed triclinic prisms, and is soluble in somewhat less than its own weight of cold water. On mixing solutions of equal molecules of the zincic and calcic salts, crystalline crusts of the difficultly soluble double salt, $(C_3H_5O_3)_2Zn,(C_3H_5O_3)_2Ca$, separate. All salts of hydracrylic acid lose water when heated to 180°–200°, and are converted into a mixture of salts of acrylic acid, $C_3H_4O_2$, and diacrylic acid, $C_6H_8O_4$.

746. If β-iodo-propionic acid be heated with ammonia solution, it yields *β-amido-propionic acid*, $C_3H_5(NH_2)O_3$ (or doubled), isomeric with alanine, which crystallises in colourless monoclinic prisms. It is readily soluble in water, difficultly in alcohol, sublimes at 170° on careful heating, and carbonises at higher temperatures.

Hydroxy-butyric Acids, $C_4H_8O_3$.

747. Four isomeric bodies of this formula have been obtained.

1. *α-Hydroxy-butyric Acid.*—On heating butyric acid for some time with a molecule of bromine to 120°–130° in sealed glass tubes, there is formed principally *α-brom-butyric acid*, $CH_3.CH_2.CHBr.CO.OH$, as a non-crystallisable oily liquid, which boils at 217° with partial decomposition, and yields an ethylic salt boiling at 172°. On heating the solutions of its alkaline salts, they are decomposed into metallic bromide and *α-hydroxy-butyric acid*, $CH_3.CH_2.CH(OH).CO.OH$, which

is purified by conversion into the zinc salt, very difficultly soluble in cold water, and the free acid separated therefrom in the usual manner. It crystallises in starlike groups of needles or prisms, melts at 43°–44°, and deliquesces in air. At higher temperatures it loses water and is converted into its ethereal anhydrides. Its zinc salt has the formula $(C_4H_7O_3)_2Zn,2H_2O$.

By decomposition of α-brom-butyric acid with ammonia it yields *amido-butyric acid*,

$$\begin{array}{l} CH_3.CH_2.CH.NH_2 \\ \qquad\qquad | \quad |\diagdown \\ \qquad\quad CO.O\ H \end{array}$$

, corresponding to glycocine and alanine, which crystallises in small needles and leafy crystals.

2. β-*Hydroxy-butyric acid*, $CH_3.CH(OH).CH_2.CO.OH$, is formed by oxidation of its aldehyde, aldol (§ 656). It is prepared synthetically from propylene hydrate chloride (§ 496) by heating with potassic cyanide and boiling the resulting solution of propylene hydrate cyanide, $CH_3.CH(OH).CH_2.CN$, with potassic hydrate.

It is most readily obtained by the action of water and sodium amalgam on ethylic aceto-acetate:

$$CH_3.CO.CH_2.CO.OC_2H_5 + Na_2 + 2H_2O$$
$$= CH_3.CH(OH).CH_2.CO.ONa + NaOH + HO.C_2H_5.$$

Its sodic salt crystallises from nearly absolute alcohol in fine prisms, which deliquesce in air. The calcic, zincic, and plumbic salts are amorphous, very soluble in water and also in alcohol.

At higher temperatures it decomposes into water and α-crotonic acid:

$$CH_3.CH(OH).CH_2.CO.OH = CH_3.CH:CH.CO.OH + H_2O.$$

3. γ-*Hydroxy-butyric acid*, $CH_2(OH).CH_2.CH_2.CO.OH$, obtained by action of baric hydrate on succinic aldehyde; it yields succinic acid on oxidation.

4. α-*Hydroxy-isobutyric acid*, $(CH_3)_2:C(OH).CO.OH$, also termed butyl lactic acid, *dimeth-oxalic acid*, or *acetonic acid*, is prepared by several methods.

Isobutyric acid is converted into α-*brom-isobutyric acid* by heating to 140° with bromine. This is crystalline, melts at 45°, and decomposes on distillation. When mixed with a small quantity of water it becomes oily, probably from formation of the trihydrate:

$$(CH_3)_2CBr.C(OH)_3,$$

but again solidifies after some time in a dry vacuum; it is but little soluble in cold water. By boiling with alkalies it is converted into α-oxyisobutyric acid.

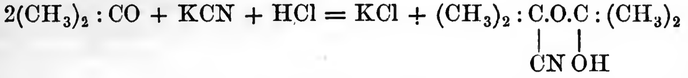
As dimeth-oxalic acid this latter is obtained by heating oxalic acid with methylic iodide and zinc (§ 705, 8), as acetonic acid from acetone, hydrocyanic and hydrochloric acids (§ 705, 6), as butyl lactic acid by oxidation of isoamylene glycol with nitric acid.

α-Hydroxy-isobutyric acid crystallises in colourless soluble prisms, which melt at 79° and sublime even at 50° in needles. It evaporates so readily in aqueous vapour that nothing is left on evaporation of an aqueous solution. By gentle oxidation it is first converted into acetone and carbonic anhydride. Its salts are all crystalline, and its zinc salt, like those of all α-oxy-acids, is very difficultly soluble in cold water.

748. *Nitrile* and *urea derivatives* of α-hydroxy-isobutyric acid can be prepared from acetone.

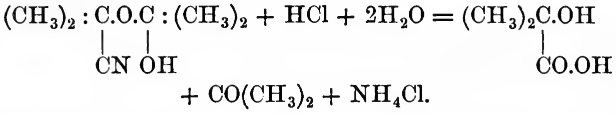
The latter unites directly with anhydrous hydrocyanic acid to form the liquid nitrile, $(CH_3)_2:C(OH).CN$, which on distillation is resolved into its components, similarly to ethylidene hydrate cyanide (§ 712).

If acetone be mixed with finely powdered potassic cyanide, and hydrochloric acid added slowly until all the latter is decomposed, the nascent elements of a molecule of hydrocyanic acid unite with two molecules of acetone, yielding *diacetone-cyanhydrin :*



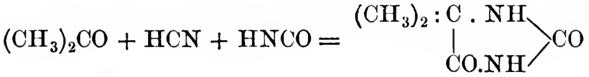
$$2(CH_3)_2:CO + KCN + HCl = KCl + (CH_3)_2:\underset{\substack{|\\ CN}}{C}.O.\underset{\substack{|\\ OH}}{C}:(CH_3)_2$$

This latter crystallises in beautiful brilliant prisms, which sublime readily, melt above 130°, and are resolved by strong acids into ammonia, acetone, and α-oxyisobutyric acid :

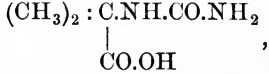


$$(CH_3)_2:\underset{\substack{|\\ CN}}{C}.O.\underset{\substack{|\\ OH}}{C}:(CH_3)_2 + HCl + 2H_2O = (CH_3)_2\underset{\substack{|\\ CO.OH}}{C}.OH + CO(CH_3)_2 + NH_4Cl.$$

A mixture of acetone with potassic cyanide and isocyanate yields, on treatment with hydrochloric acid, *acetonyl urea*, corresponding to hydantoïn (§ 724), and lactyl urea (§ 739) :



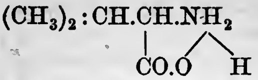
$$(CH_3)_2CO + HCN + HNCO = \left.\begin{array}{l}(CH_3)_2:C\,.\,NH\\ \qquad\ \ |\\ \qquad CO.NH\end{array}\right\rangle CO$$

It is crystalline, melts at 175°, sublimes in fine brilliant needles on careful heating, and on heating with baric hydrate solution yields the amorphous salt of *acetonuramic acid*,  $(CH_3)_2:\underset{\substack{|\\ CO.OH}}{C}.NH.CO.NH_2$, corresponding to hydantoïc acid, which in the free state decomposes into water and acetonyl urea. By boiling with acids the latter is resolved into ammonia, carbonic and α-oxyisobutyric acid.

Hydroxy-valeric Acids, $C_5H_{10}O_3$.

749. Only three of the numerous theoretically possible oxyvaleric acids are known.

1. *α-Hydroxy-isovaleric acid*, $(CH_3)_2:CH.CH(OH).CO.OH$, is formed from *α-brom-isovaleric acid*, $(CH_3)_2:CH.CHBr.CO.OH$ (obtained by heating isovaleric acid with bromine), by boiling with moist argentic oxide. It crystallises in large colourless tables, melting at 80° and slowly subliming below 100°, which dissolve readily in water, alcohol, and ether. A mixture of chromic and sulphuric acids oxidises it to isobutyric acid, carbonic anhydride, and water. By boiling ammonic α-brom-isovalerate with ammonia, *α-amido-isovaleric acid*,



$$\begin{array}{l}(CH_3)_2:CH.CH.NH_2\\ \qquad\quad | \quad \diagup\diagdown\\ \qquad CO.O \quad\; H\end{array}$$

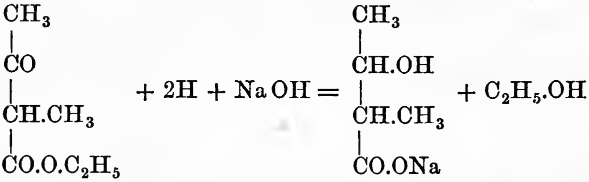
, is formed, which crystallises in colourless leaves, somewhat sublimable. It behaves towards acids and bases in similar manner to alanine, glycocine, &c. Apparently the same body has been prepared, under the name of *butalanine,* from the spleen and pancreas gland of oxen.

2. *Eth-meth-oxalic acid,* $\genfrac{}{}{0pt}{}{CH_3.CH_2}{CH_3}\!\!>\!C(OH).CO.OH$, the α-hydroxy substitution product of eth-meth-acetic acid, is obtained by heating together a mixture of ethylic oxalate, ethylic iodide, and methylic iodide with zinc, in the form of its ethylic salt (boiling point 165°). This, on saponification with alkalies, decomposition of the salt with sulphuric acid, and extraction with ether, yields the free acid in readily soluble crystals, melting at 63°.

3. *β-Hydroxy α-methyl butyric acid :*

$$CH_3.CH(OH).CH(CH_3).CO.OH.$$

The sodic salt of this acid is obtained by the action of sodium amalgam on an aqueo-alcoholic solution of ethylic aceto-meth-acetate :



$$\begin{array}{l}CH_3\\ |\\ CO\\ |\\ CH.CH_3\\ |\\ CO.O.C_2H_5\end{array} + 2H + Na\,OH = \begin{array}{l}CH_3\\ |\\ CH.OH\\ |\\ CH.CH_3\\ |\\ CO.ONa\end{array} + C_2H_5.OH$$

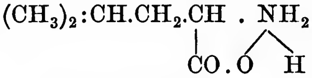
The free acid does not crystallise, nor has it been as yet obtained anhydrous, as on drying it is gradually converted into a dehydro-acid. On distillation it yields a dimeth-acrylic acid, $CH_3.CH:C(CH_3).CO.OH$.

Hydroxy-caproic Acids, $C_6H_{12}O_3$.

750. 1. *α-Oxyisocaproic acid, leucic acid :*

$$(CH_3)_2:CH.CH_2.CH(OH).CO.OH.$$

Isovaleric aldehyde ammonia yields, on treatment with hydrocyanic and hydrochloric acid, *α-amido-isocaproic acid :*



$$\begin{array}{l}(CH_3)_2:CH.CH_2.CH\;.\;NH_2\\ \qquad\qquad\qquad\quad\;\; | \quad \diagup\diagdown\\ \qquad\qquad\qquad\;\; CO\,.\,O \quad H\end{array}$$

which is converted into the oxyacid by treatment with nitrous acid. The oxyacid crystallises in colourless needles, readily soluble and melting at 73°. Its salts are mostly difficultly soluble.

A body of great physiological importance, known as *leucine* and obtained as a decomposition product of albuminoid bodies, is probably identical with α-amido-caproic acid. It is obtained from nearly all proteoids and from gelatine (in the latter case together with glycocine) by putrefaction, by action of pancreas ferment, and by boiling with alkalies and strong acids ; it occurs in small quantity in some animal organs.

From the true albuminoids, as also from horn and elastine, leucine is invariably obtained, together with the more difficultly soluble, and therefore readily separable, tyrosine. Elastine gives the greatest yield. The dried cervical ligament of the ox, reduced to the finest possible state of division, is placed in a hot mixture of two parts sulphuric acid and three parts water, and heated for several hours in a vessel provided with an inverted condenser. So much milk of lime is then added that the sulphuric acid is exactly neutralised, and, after dilution with six times its volume of water, the mixture is filtered. The filtrate is mixed with some more milk of lime, boiled for several hours, and the hot filtered liquid neutralised with sulphuric acid. The clear liquid, separated from the calcic sulphate, is then evaporated to a thin syrup, and the mixture of tyrosine and leucine separated by crystallisation from water.

Leucine crystallises in white nacreous leaves, of fatty feeling, soluble in 27 parts of cold water and in 1,040 parts of cold alcohol. It melts at 170°, and sublimes in part unchanged. On stronger heating it decomposes into carbonic anhydride and amylamine.

Leucic acid, prepared from leucine by action of nitrous acid, so closely resembles α-oxycaproic acid that they are held to be identical.

2. *α-Hydroxy-dieth-acetic acid*, or *dieth-oxalic acid:*

$$(CH_3.CH_2)_2:C(OH).CO.OH,$$

is prepared from ethylic oxalate and ethylic iodide by heating with zinc. It is crystalline, readily soluble, sublimes slowly at 50°, melts at 74°, and is oxidised by chromic and sulphuric acids to diethyl ketone, carbonic anhydride, and water.

3. *β-Hydroxy α-ethyl butyric acid:*

$$CH_3.CH(OH).CH(C_2H_5)CO.OH,$$

obtained by action of nascent hydrogen, &c., on ethylic aceto-ethyl acetate, is a colourless syrup, yields a dehydro-acid on evaporation, and on distillation gives meth-eth-acrylic acid:

$$CH_3.CH:C(C_2H_5).CO.OH.$$

Hydroxy-œnanthoic Acids, $C_7H_{14}O_3$.

750*a*. *α-Hydroxy-isœnanthoic acid:*

$$(CH_3)_2.CH_2.CH_2.CH_2.CH(OH).CO.OH,$$

obtained as ethylic salt in the action of zinc on a mixture of ethylic oxalate and isoamylic iodide; the free acid crystallises in nacreous scales, fusing at 60·5°.

β-Hydroxy α-methyl-ethyl butyric acid:

$$CH_3.CH(OH).C(CH_3)(C_2H_5).CO.OH,$$

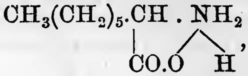
is obtained by the action of nascent hydrogen, &c., on ethylic aceto-eth-meth-acetate; it requires further investigation.

751. Of higher members of the series three *oxycaprylic acids*, $C_8H_{16}O_3$, have been prepared.

α-Oxycaprylic acid:

$$CH_3.CH_2.CH_2.CH_2.CH_2.CH_2.CH(OH)CO.OH,$$

is formed, similarly to alanine, by mixing œnanthol (§ 400) with anhydrous hydrocyanic acid and succeeding distillation of the product with strong hydrochloric acid, &c. It crystallises in colourless leafy crystals, melting at 96·5°, difficultly soluble in water, readily in alcohol and ether.

The corresponding *amido-caprylic acid*,  $CH_3(CH_2)_5.CH.NH_2$, $CO.O$, H, obtained from œnanthol-ammonia by treatment with hydrocyanic and hydrochloric acids, crystallises in white nacreous leaves of neutral reaction, which sublime unchanged.

Diisoprop-oxalic acid, $\left(\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CH\right)_2C(OH).CO.OH$, is prepared by heating ethylic oxalate with isopropylic iodide and zinc.

The ethylic salt first formed boils at 200°. The free acid crystallises in colourless needles, which melt at 110°–111°, and are somewhat sublimable. It is difficultly soluble in cold water, readily in alcohol and ether. The calcic and baric salts are readily soluble even in cold water; the zinc salt forms a flocculent precipitate.

β-Hydroxy α-diethyl butyric acid, $CH_3.CH(OH).C(C_2H_5)_2.CO.OH$, obtained by the action of nascent hydrogen, &c., on ethylic acetodiethyl acetate, is a thick liquid, difficultly soluble in water; on heating it yields ethylic aldehyde and dieth-acetic acid.

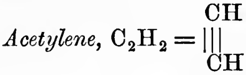
$C_{12}H_{24}O_3$. *Diisoamyl hydroxy-acetic acid:*

$$[(CH_3)_2CH_2.CH_2.CH_2]_2:C(OH).CO.OH,$$

obtained at the same time as α-hydroxy-isœnanthoic acid, crystallises in colourless satiny fibres, melting at 122°.

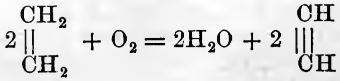
Compounds of the Double Aldehyde Radicals, $C_nH_{2n}(CH:)_2$.

752. The first hydrocarbon nucleus of the constitution of a radical of a double aldehyde contains two carbon atoms, C_2H_2. It occurs in the free state with triple union of the carbon atoms and forms



Acetylene, $C_2H_2 = \begin{matrix}CH\\|||\\CH\end{matrix}$

Acetylene is the only hydrocarbon that can be prepared directly from its free elements, this occurring when the electric arc passes between carbon poles in an atmosphere of hydrogen. It is formed from nearly all organic compounds at a strong red heat, and therefore occurs regularly in coal gas. It can be obtained from this latter in considerably larger quantity by incomplete combustion, whether this be effected by deficiency of oxygen or by reduction of the temperature of the flame, e.g.



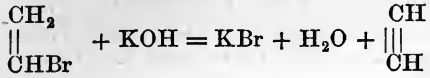
$$2\begin{matrix}CH_2\\||\\CH_2\end{matrix} + O_2 = 2H_2O + 2\begin{matrix}CH\\|||\\CH\end{matrix}$$

or

$$4CH_4 + 3O_2 = 6H_2O + 2C_2H_2.$$

Calcic and potassic carbides (bye product of the preparation of potassium), when heated with water, evolve acetylene.

The richest yield is obtained by passing the vapour of brom-ethylene (§ 649) into hot alcoholic potassic hydrate:



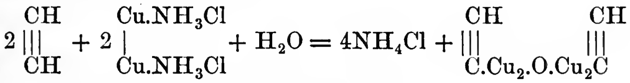
$$\begin{array}{l}CH_2\\ \| \\ CHBr\end{array} + KOH = KBr + H_2O + \begin{array}{l}CH\\ ||| \\ CH\end{array}$$

It is also obtained by the action of the 'zinc copper couple' on chloroform, bromoform, and iodoform, or by the action of zinc on chloral hydrate.

Acetylene is a colourless gas, liquefiable at a pressure of 83 atmospheres at 18°, of strongly disagreeable odour, and which burns with a very luminous flame.

Extremely characteristic for acetylene, *as for all hydrocarbons which contain the triply united terminal group* $\vdots CH$, is the replaceability of the hydrogen atom by certain metals. On passing acetylene gas over heated alkali metals, hydrogen is evolved, and voluminous colourless compounds are formed, e.g. $CH \vdots CNa$ and $CNa \vdots CNa$, which are violently decomposed by water into alkaline hydrate and acetylene.

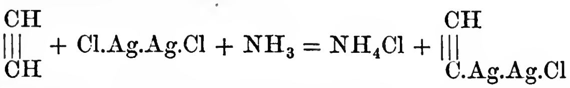
The replacement is effected still more readily by silver or copper. If a gaseous mixture containing acetylene be passed through an ammoniacal solution of cuprous chloride, a red precipitate of very explosive nature is produced:



$$2\begin{array}{l}CH\\ ||| \\ CH\end{array} + 2\begin{array}{l}Cu.NH_3Cl\\ | \\ Cu.NH_3Cl\end{array} + H_2O = 4NH_4Cl + \begin{array}{l}CH \qquad\qquad CH\\ ||| \qquad\qquad\ ||| \\ C.Cu_2.O.Cu_2C\end{array}$$

This precipitate is *diacetylene cuprous oxide.*

Similarly, acetylene gives, with a strongly ammoniacal solution of argentic nitrate, a white precipitate of *diacetylene argentoxide,* $(H.C \vdots C.Ag.Ag)_2O$; with a weak ammoniacal solution of argentic chloride, *acetylene argento-chloride:*



$$\begin{array}{l}CH\\ ||| \\ CH\end{array} + Cl.Ag.Ag.Cl + NH_3 = NH_4Cl + \begin{array}{l}CH\\ ||| \\ C.Ag.Ag.Cl\end{array}$$

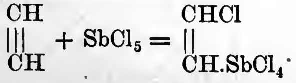
These silver compounds also explode with great violence when in the dry condition, either by friction or by heating.

Both copper and silver compounds evolve acetylene when heated with hydrochloric acid:

$$(CH \vdots C.Cu.Cu)_2O + 4HCl = 2CH \vdots CH + 2Cu_2Cl_2 + OH_2$$

$$CH.C.Ag.Ag.Cl + HCl = CH \vdots CH + Ag_2Cl_2.$$

Acetylene is absorbed by antimonic chloride, yielding large leafy crystals, apparently of a direct compound:



$$\begin{array}{l}CH\\ ||| \\ CH\end{array} + SbCl_5 = \begin{array}{l}CHCl\\ \| \\ CH.SbCl_4\end{array}$$

which at higher temperatures decomposes into antimonious chloride and *acetylene dichloride:*

$$CHCl:CHSbCl_4 = CHCl:CHCl + SbCl_3.$$

On heating the antimonic chloride compound with excess of antimonic chloride, *acetylene tetrachloride* distils as a colourless liquid, boiling at 147°:

$$CHCl:CHSbCl_4 + SbCl_5 = 2Sb.Cl_3 + CHCl_2.CHCl_2.$$

Acetylene dichloride is a colourless liquid, which boils at 55°, on heating its vapour to 360° decomposes into hydrochloric acid and carbon:

$$C_2H_2Cl_2 = 2HCl + C_2,$$

and on heating with alcoholic potassic hydrate yields potassic chloride and acetate:

$$C_2H_2Cl_2 + 3KOH = 2KCl + C_2H_3O.OK + H_2O.$$

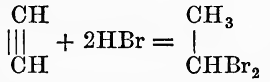
Notwithstanding the different boiling points assigned to these compounds, acetylene dichloride and tetrachloride appear to be identical with dichlor ethylene and dichlor ethylene dichloride (§ 473), the lower boiling points of these latter being due to their not being completely pure.

These chlorides cannot be prepared by the direct action of chlorine on acetylene, as explosion with separation of carbon ensues on mixing the two gases.

Acetylene is absorbed by *cold* bromine, and yields the liquid compounds *acetylene dibromide*, $CHBr:CHBr$, and *acetylene tetrabromide*, $CHBr_2.CHBr_2$.

It unites with iodine at 100°, forming the crystalline acetylene diiodide $CHI:CHI$, which melts at about 70°.

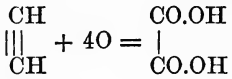
It also unites directly with hydrobromic and hydriodic acids. The first yields ethylidene dibromide (§ 379):



$$\begin{array}{c} CH \\ ||| \\ CH \end{array} + 2HBr = \begin{array}{l} CH_3 \\ | \\ CHBr_2 \end{array}$$

the latter the two liquid compounds iodethylene, $CH_2:CHI$ (§ 475), and ethylidene diiodide, $CH_3.CHI_2$ (boiling point 182°).

Nascent hydrogen converts acetylene into ethylene; this is best effected by bringing together diacetylene cuproso-oxide, zinc, and aqueous ammonia. Strong oxidising agents (potassic permanganate) convert acetylene into oxalic acid:

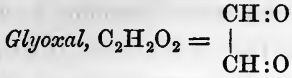


$$\begin{array}{c} CH \\ ||| \\ CH \end{array} + 4O = \begin{array}{l} CO.OH \\ | \\ CO.OH \end{array}$$

753. *Dichlor aldehyde*, $C_2H_2Cl_2O = CHCl_2.CHO$. The chief product of the action of chlorine gas on acetal (§ 405) is *dichlor acetal*, $CHCl_2.CH(OC_2H_5)_2$, a liquid boiling at 180°, which by distillation with concentrated sulphuric acid yields *dichlor aldehyde*:

$$CHCl_2.CH(OC_2H_5)_2 + 2H_2SO_4 = 2(C_2H_5)HSO_4 + H_2O \\ + CHCl_2.CHO.$$

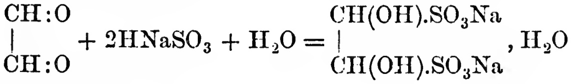
Dichlor aldehyde is a clear liquid, boiling between 88° and 90°, insoluble in water; after some time it is transformed into the solid polymeric *paradichlor aldehyde*, the latter being reconverted into dichlor aldehyde at 120°. By treatment with phosphoric chloride dichlor aldehyde yields tetrachlor ethane (§ 708), by oxidation dichlor acetic acid.



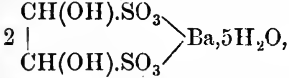
754. *Glyoxal*, $C_2H_2O_2 = \begin{array}{l} CH:O \\ | \\ CH:O \end{array}$

This is formed, together with glycollic acid and glyoxalic acid, by the moderated oxidation of ethylene glycol and ethylic alcohol with nitric acid (§ 712). The preparation is effected as there described, only, instead of evaporating the contents of the cylinder in small portions (whereby the glyoxal is further oxidised by still unchanged nitric acid into glyoxalic and oxalic acids), the whole oxidation product is heated for some hours in a vessel provided with an inverted condenser, whereby the nitric acid is destroyed by the ethylic alcohol and acetic aldehyde present. After neutralising with chalk, and separating the salts with alcohol, the alcoholic filtrate is evaporated on the water bath to a thick syrup, and again treated with absolute alcohol, whereby some more calcic glycollate separates. The alcoholic extract is then again evaporated, and mixed with several times its volume of a saturated solution of hydric sodic sulphite, and allowed to stand for a day in a cool place. It then yields a large colourless crystalline precipitate of

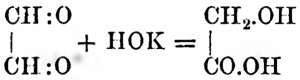
Glyoxal sodic sulphite, or acetylene dihydrate disodic sulphite:



$$\begin{array}{l} CH:O \\ | \\ CH:O \end{array} + 2HNaSO_3 + H_2O = \begin{array}{l} CH(OH).SO_3Na \\ | \\ CH(OH).SO_3Na \end{array}, H_2O$$

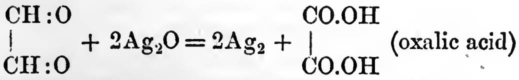


A warm saturated solution of this body gives, on addition of baric chloride, crystalline crusts of the difficultly soluble baric compound $2\left.\begin{array}{l} CH(OH).SO_3 \\ | \\ CH(OH).SO_3 \end{array}\right\rangle Ba,5H_2O$, from which, by addition of the requisite quantity of sulphuric acid, glyoxal is formed, sulphurous anhydride being evolved. On evaporation of the filtered solution, *glyoxal* is left as an amorphous deliquescent mass, also readily soluble in alcohol and ether. Like all aldehydes, it is converted by alkalies into a yellow resinous mass, partially with formation of glycollic acid:



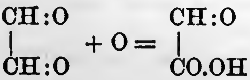
$$\begin{array}{l} CH:O \\ | \\ CH:O \end{array} + HOK = \begin{array}{l} CH_2.OH \\ | \\ CO.OH \end{array}$$

and reduces the oxides of noble metals, being itself oxidised to glyoxalic and oxalic acids:



$$\begin{array}{l} CH:O \\ | \\ CH:O \end{array} + 2Ag_2O = 2Ag_2 + \begin{array}{l} CO.OH \\ | \\ CO.OH \end{array} \text{(oxalic acid)}$$

Dilute nitric acid oxidises it principally to glyoxalic acid:



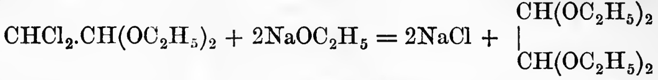
$$\begin{array}{l} CH:O \\ | \\ CH:O \end{array} + O = \begin{array}{l} CH:O \\ | \\ CO.OH \end{array}$$

On treatment of a solution of glyoxal in strong acetic acid with hydrochloric acid, a white amorphous mass is precipitated, which is insoluble in water, ether, chloroform, &c. It has the composition $C_{12}H_{14}O_{13}$, and must be produced according to the equation:

$$6C_2H_2O_2 + H_2O = C_{12}H_{14}O_{13},$$

and is therefore termed *hexaglyoxal hydrate.* Its constitution is unknown. Treated with acetylic chloride, a hydrogen atom is replaced by acetyl and an insoluble white amorphous powder, *hexaglyoxal acetate*, $C_{12}H_{13}(C_2H_3O)O_{13}$, formed.

Dichlor acetal (§ 753) is converted by long heating with sodic ethylate into *glyoxal acetal:*



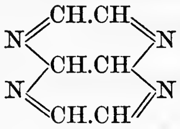
$$CHCl_2.CH(OC_2H_5)_2 + 2NaOC_2H_5 = 2NaCl + \begin{array}{l}CH(OC_2H_5)_2\\|\\CH(OC_2H_5)_2\end{array}$$

a colourless liquid, lighter than water, boiling at 180°.

755. When glyoxal is dissolved in aqueous ammonia, two basic compounds are slowly formed.

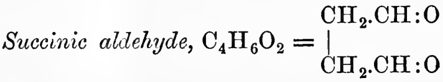
Glycosine, $C_6H_6N_4$, separates in small needles, insoluble in water, and yields soluble crystalline salts with two equivalents of acid. The platino-chloride has the formula $C_6H_6N_4,2HCl,PtCl_4$. Without doubt glycosine belongs to the nitrile bases of the aldehyde radicals (comp. §§ 423 and 424), and its formation may be represented by the equation:

$$3CHO.CHO + 4NH_3 = 6H_2O +$$



Glyoxaline, $C_3H_4N_2$, or more probably $C_6H_8N_4$, is readily soluble in water. Its platino-chloride is $C_6H_8N_4,2HCl,PtCl_4$. Its formation from glyoxal has not yet been completely explained.

756. No member of the group containing three carbon atoms is known; the four-carbon member



$$\textit{Succinic aldehyde}, C_4H_6O_2 = \begin{array}{l}CH_2.CH:O\\|\\CH_2.CH:O\end{array}$$

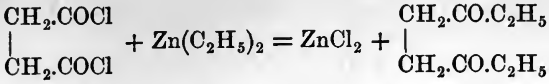
is prepared from succinic acid (which it again yields on oxidation) by first heating with phosphoric chloride, when the dichloride, $\begin{array}{l}CH_2.COCl\\|\\CH_2.COCl\end{array}$, is obtained, which on further treatment with acetic acid and sodium amalgam exchanges its chlorine for hydrogen. Succinic aldehyde is liquid, boils at 201°–203°, is soluble in water, and yields a crystalline compound with hydric sodic sulphite.

DERIVATIVES OF THE DOUBLE KETONE RADICALS.

757. Only a single body of this class is known with certainty—*ethylene diethyl diketone:*

$$C_8H_{14}O_2 = C_2H_5.CO.CH_2.CH_2.CO.C_2H_5.$$

It is prepared by action of succinyl chloride on zinc ethyl, which is diluted with benzene, in order to moderate the violence of the reaction :



$$\begin{array}{l}CH_2.COCl\\ |\\ CH_2.COCl\end{array} + Zn(C_2H_5)_2 = ZnCl_2 + \begin{array}{l}CH_2.CO.C_2H_5\\ |\\ CH_2.CO.C_2H_5\end{array}$$

It is a faint yellow, mobile, oily liquid, heavier than water.

Derivatives of Ketone Aldehyde Radicals.

758. To this group belong some hydrocarbons, $C_{n'}H_{2n'+1}.C\vdots H$, homologous with acetylene, and their derivatives.

Allylene, $CH_3.C\vdots CH$.

759. Allylene is prepared (analogously to the preparation of acetylene from the halogen substitution products of ethylene) by the action of an alcoholic solution of sodic ethylate on chlor- and brom-propylene (§ 658) :

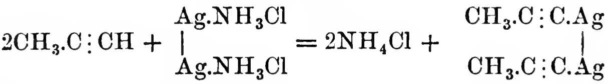
$$CH_3.CCl:CH_2 + NaOC_2H_5 = NaCl + HO.C_2H_5 + CH_3.C\vdots CH,$$

and by the decomposition of its tetrachloride, dichlor-acetone chloride, with sodium :

$$CH_3.CCl_2.CHCl_2 + 2Na_2 = 4NaCl + CH_3.C\vdots CH.$$

It is a colourless gas which gives precipitates in ammoniacal solutions of cuprous and argentic compounds, of similar constitution to the acetylene compounds. The cuprous precipitate is siskin green, and silver compound white crystalline and has the formula :

$$(C_3H_4)_2Ag_2:$$



$$2CH_3.C\vdots CH + \begin{array}{l}Ag.NH_3Cl\\ |\\ Ag.NH_3Cl\end{array} = 2NH_4Cl + \begin{array}{r}CH_3.C\vdots C.Ag\\ |\\ CH_3.C\vdots C.Ag\end{array}$$

When treated with acids allylene is evolved.

Allylene yields two colourless oily compounds with bromine, *allylene dibromide*, $CH_3.CBr:CHBr$, boiling at 130°–131°, and of sp. gr. 2·05, and *allylene tetrabromide*, $CH_3.CBr_2.CHBr_2$, of sp. gr. 2·94, which cannot be distilled unchanged. Allylene combines slowly with iodine, forming allylene diiodide, $CH_3.CI.CHI$, a liquid boiling at 198°.

Hydrochloric and hydrobromic acid are absorbed directly by allylene with formation of dihaloids of the acetone radical. Hydrochloric acid yields dimethyl carbin-dichloride (§ 445) :

$$CH_3.C\vdots CH + 2HCl = CH_3.CCl_2.CH_3,$$

hydrobromic acid giving, in addition to the corresponding dimethyl carbin-dibromide, $CH_3.CBr.CH_3$, also propenyl bromide :

$$CH_3.C\vdots CH + HBr = CH_3.CH.CHBr,$$

boiling at 48° and isomeric with brom-propylene.

With hydriodic acid it forms an oil isomeric with propylene diiodide, which has at 0° sp. gr. 2·44, and boils with decomposition at 147°–148°. It is probably *dimethyl carbin-diiodide*, $CH_3.CI_2.CH_3$.

Allylene dichloride, $CH_3.CCl:CHCl$, has not yet been prepared from allylene, but is obtained, together with the isomeric dichlor-glycid, by action of potassic hydrate on methyl chlor-acetol:

$$CH_3.CCl_2.CH_2Cl + KOH = KCl + H_2O + CH_3.CCl:CHCl.$$

It is a liquid boiling at 75°.

760. The dihalogenised acetones obtained by direct substitution from acetone may be considered amongst the allylene derivatives.

Unsymmetrical dichlor-acetone, $CH_3.CO.CHCl_2$, obtained by action of chlorine on acetone, is a liquid boiling at 120° and of sp. gr. 1·236. Phosphoric chloride converts it into the so-called *dichlor-acetone chloride*:

$$CH_3.CO.CHCl_2 + PCl_5 = POCl_3 + CH_3.CCl_2.CHCl_2,$$

which is without doubt *allylene tetrachloride*. It boils at 153° and has sp. gr. 1·47 at 13°.

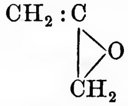
761. *Propyl acetylene*, $C_5H_8{=}CH_3.CH_2.CH_2.C\vdots CH$, is the only one of the numerous hydrocarbons of the formula C_nH_{2n-2} truly homologous with allylene. It is obtained by the action of alcoholic potassic hydrate upon the dichloride of the methyl-propyl ketone radical:

$$CH_3.CH_2.CH_2.CCl_2.CH_3 + 2KOH = 2KCl + 2H_2O$$
$$+ CH_3.CH_2.CH_2.C\vdots CH.$$

It is a liquid boiling at 50°, which gives a yellow precipitate in an ammoniacal solution of cuprous chloride and a white precipitate with the corresponding silver compound.

DERIVATIVES OF THE ALDEHYDE DOUBLE ALCOHOL RADICALS, C_nH_{2n-2}.

762. Of this group scarcely anything is known but unsaturated compounds; namely, the aldehydes of the unsaturated alcohols $C_nH_{2n-1}OH$. The first member of the group is acroleïn, the aldehyde of allylic alcohol; but, as it differs greatly in its chemical behaviour from the true aldehydes containing the group $CH:O$, it is doubtful whether the formula $CH_2:CH.CH:O$ should be assigned to it, or if its properties do not correspond better with the expression:

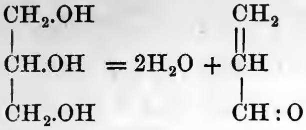


Its relations to hydracrylic and glyceric acids agree with the latter formula, but as the question is still unsettled it will be viewed here as a true aldehyde.

Acroleïn, $C_3H_4O = CH_2:CH.CH:O$.

763. Acroleïn is formed by the careful oxidation of allylic alcohol, by the dry distillation of glycerin and its salts (the fats), and by the action of bromine on acetone.

To prepare it one part of anhydrous glycerine is mixed with two parts of hydric potassic sulphate and the mixture submitted to dry distillation. The decomposition proceeds according to the equation :



$$\begin{array}{l} CH_2.OH \\ | \\ CH.OH \\ | \\ CH_2.OH \end{array} = 2H_2O + \begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ CH:O \end{array}$$

The distillate is then carefully mixed with calcic chloride, some plumbic oxide added to remove any admixed sulphurous acid, and then rectified on the water bath.

Acroleïn is a thin colourless liquid, boiling at 52°, of most irritating odour. It is lighter than water and requires about forty parts of the latter for solution. It mixes with alcohol and ether in every proportion. On keeping it is transformed into a white amorphous substance, *disacryl*, a polymer of unknown molecular weight and structure, from which acroleïn cannot be regained.

It does not yield a crystalline compound with acid alkali sulphites. Nascent hydrogen converts it into allylic alcohol, alkalies resinify it, argentic oxide oxidises it to acrylic acid.

On passing hydrochloric acid into acroleïn, an oil is obtained solidifying in needles, $C_3H_4O.HCl$, which on distillation alone is resolved into its components, but with potassic hydrate yields metacroleïn.

Metacroleïn, probably $C_9H_{12}O_3 = 3C_3H_4O$, forms colourless crystals insoluble in water, melting as 50° and boiling at 170°. At somewhat higher temperature (in part also during distillation) the vapours dissociate into acroleïn.

Phosphoric chloride reacts with acroleïn according to the equation :

$$C_3H_4O + PCl_5 = POCl_3 + C_3H_4Cl_2.$$

The resulting dichloride is a mixture of two isomeric liquid compounds, of which one, termed *acrol chloride*, boils at 84°, and probably has the formula $CH_2 : CH.CHCl_2$, whilst the other is *dichlor glycid* (§ 767).

Acroleïn unites directly with two atoms of chlorine or bromine. Nitric acid converts the dibromide, $C_3H_4Br_2O$, into a polymeric compound, which crystallises in prisms or leaves and melts at 59°.

Acroleïn and ammonia react in alcoholic solution to form a brown or yellow amorphous compound, *acroleïn ammonia*, which, however, does not correspond to the alkylidene hydrate amides, but is homologous with oxytetraldine (§ 424) :

$$2C_3H_4O + NH_3 = H_2O + C_6H_9NO.$$

It forms amorphous salts with acids, and decomposes into picoline and water on dry distillation.

764. *Isodichlor glycid*, or *β-chlor-allyl chloride*, $CH_2Cl.CH:CHCl$, isomeric with allylene dichloride and acrol chloride, is formed, together with dichlor glycid, when glyceryl trichloride is decomposed by alkalies, as a colourless liquid, boiling at 109°. It is formed in larger quantity by heating dichlor-hydrin (§ 679) with phosphoric anhydride :

$$CH_2Cl.CH(OH).CH_2Cl + P_2O_5 = 2HPO_3 + CH_2Cl.CH:CHCl.$$

It combines directly with chlorine, forming $CH_2Cl.CHCl.CHCl_2$.

α-Crotonic Aldehyde, $C_4H_6O = CH_3.CH:CH.CHO$.

765. *α-Crotonic aldehyde*, also known as *crotonic aldehyde*, is obtained from acetic aldehyde by long heating at 100° with a concentrated solution of potassic acetate, or with zincic chloride and a little water :

$$2CH_3.CHO = H_2O + CH_3.CH:CH.CHO,$$

and from aldol (§ 656) by distillation :

$$CH_3.CH(OH).CH_2.CHO = H_2O + CH_3.CH:CH.CHO.$$

Crotonic aldehyde is a mobile, colourless liquid, which after momentary fruity odour acts on the eyes and nose like acroleïn. It boils at 104°–105°, is somewhat soluble in water, and by oxidation (slowly in air, rapidly by argentic oxide) is converted into α-crotonic acid. With phosphoric pentachloride it yields *crotonal dichloride :*

$$CH_3.CH:CH.CHCl_2,$$

an oil boiling at 125°–127°, and unites directly with hydrochloric acid, forming chlor-butyric aldehyde :

$$CH_3.CH:CH.CHO + HCl = CH_3.CH_2.CHCl.CHO.$$

DERIVATIVES OF KETONE DOUBLE ALCOHOL RADICALS.

Isallylene, $CH_2:C:CH_2$, *and Glycid Compounds.*

766. *Isallylene*, a gaseous hydro-carbon isomeric with allylene, and to which the formula $CH_2:C:CH_2$ has been assigned, is only prepared by the electrolysis of potassic itaconate. It gives no precipitate with ammoniacal solutions of silver salts ; it combines directly with bromine to form crystalline isallylene tetrabromide :

$$CH_2Br.CBr_2.CH_2Br.$$

Its direct relation to the following glycid compounds, though not yet shown directly, is still scarcely doubtful.

Glycid Compounds or Derivatives of α-substituted Allyl.

767. On bringing together glyceryl trichloride with powdered potassic hydrate, an energetic reaction ensues, in which a hydrogen and a chlorine atom are removed, and there is formed

Dichlor glycid, $CH_2:CCl.CH_2Cl$, or α-chlor-allyl chloride, probably the dichloride of isallylene, isomeric with allylene dichloride, isodichlor glycid, and acrol chloride. It is a mobile liquid of agreeable ethereal odour, which boils at 94° and combines with a molecule of chlorine, forming *dichlor-glycid dichloride*, $CH_2Cl.CCl_2.CH_2Cl$, of boiling point 164°. It also unites with a molecule of bromine, forming *dichlor-glycid dibromide*, $CH_2Br.CClBr.CH_2Cl$, a liquid of sp. gr. 2·1 and boiling point 221°.

By heating with six times its volume of sulphuric acid, and distillation of the product with water, it is converted into monochlor-acetone (§ 660). The process may be represented by the equations:

$$CH_2:CCl.CH_2Cl + HO.SO_2.OH = CH_3.CCl(O.SO_2.OH).CH_2Cl$$

and

$$CH_3.CCl(O.SO_2.OH).CH_2Cl + H_2O = H_2SO_4 + HCl + CH_3.CO.CH_2Cl.$$

Dibrom-glycid, $CH_2:CBr.CH_2Br$, or *α*-brom-allyl bromide, prepared from glyceryl tribromide and potassic hydrate, boils at 151°–152°.

768. When dibrom-glycid is heated with the salts of monobasic acids, it exchanges only one bromine atom—the *terminal* one—for the acid radical, and yields *a-brom-allylic salts:*

$$CH_2:CBr.CH_2Br + AgO.NO_2 = AgBr + CH_2:CBr.CH_2.O.NO_2.$$

α-Brom-allylic nitrate, boils between 140° and 150°.

$$CH_2:CBr.CH_2Br + KO.C_2H_3O = KBr + CH_2:CBr.CH_2.O.C_2H_3O.$$

α-Brom-allylic acetate, boiling point 163°–164°.

from which alkalies liberate *a-brom-allylic alcohol*, $CH_2:CBr.CH_2.OH$, as a colourless, mobile liquid of agreeable odour, sp. gr. 1·6 at 15° and boiling at 155°.

Phosphoric chloride converts the alcohol into *a-brom-allylic chloride*, or *chlor-bromglycid*, $CH_2:CBr.CH_2Cl$, which boils at 120°, and is also formed by the action of alkalies on glyceryl dichloro-bromide:

$$CH_2Cl.CHBr.CH_2Cl \text{ (§ 682).}$$

Glyceryl dibromo-ethylate (§ 685), prepared from allyl-ethyl ether and bromine, is similarly converted by alkalies into *a-bromallyl-ethyl ether*, $CH_2:CBr.CH_2.O.C_2H_5$, a colourless liquid of agreeable odour, boiling at 130°–135°, of sp. gr. 1·26 at 12°.

Dibrom-glycid also reacts with potassic sulphocyanate, forming *a-brom-allyl sulphocyanate* (comp. § 671), $CH_2:CBr.CH_2.N:CS$, which distils at about 200°, and with ammonia yields *a-brom-allyl sulphurea*, $CH_2:CBr.CH_2.NH.CS.NH_2$, as crystals melting at 110°–111°.

Symmetrical dichlor-acetone, $CH_2Cl.CO.CH_2Cl$ (comp. § 760), can also be reckoned amongst the fully saturated derivatives of isallylene. It is obtained by oxidation of dichlorhydrin (§ 679, 2) with chromic and sulphuric acids, and occurs amongst the products of direct chlorination of acetone. It crystallises in colourless rhombic tables, melts at 43°, and boils at 172°–174°.

Homologues of Isallylene.

769. Several hydrocarbons behave quite similarly to isallylene as regards their inability to precipitate ammoniacal silver and cuprous compounds, and can therefore be regarded as homologous to it.

Crotonylene, $C_4H_6 = CH_3.CH:C:CH_2$, occurs in coal gas, and can be separated therefrom in the liquid form by pressure. It is obtained, similarly to acetylene and allylene, by heating brom-butylene (§ 661) with alcoholic potassic hydrate:

$$CH_3.CH_2.CBr:CH_2 + KOH = KBr + H_2O + CH_3.CH:C:CH_2,$$

and by passing a mixture of equal volumes of acetylene and ethylene through a tube heated to dull redness:

$$CH_2:CH_2 + CH \vdots CH = CH_3.CH:C:CH_2.$$

It is a colourless liquid boiling at 20°, which unites with bromine, forming a liquid dibromide, $C_4H_6Br_2$, boiling at 150°, and a crystalline tetrabromide, $CH_3.CHBr.CBr_2.CH_2Br$.

Isovalerylene, $C_5H_8 = (CH_3)_2C:C:CH_2$, is formed from brom-isoamylene (§ 701) by alkalies. It is a liquid of garlic odour which boils between 42° and 45°. It yields only liquid compounds with bromine; namely, a dibromide, $C_5H_8Br_2$, boiling at 170°, and a tetrabromide, $C_5H_3Br_4$ or $(CH_3)_2:CBr.CBr_2.CH_2Br$, which cannot be distilled unchanged. Some higher hydrocarbons of the series C_nH_{2n-2} have been prepared in similar manner from the mono-halogen olefines, but require more investigation; e.g. *hexoylene*, C_6H_{10}, distilling between 76° and 80°.

DERIVATIVES OF THE TETRHYDRIC ALCOHOL RADICALS.

Erythrite, $C_4H_6(OH)_4 = CH_2(OH).CH(OH).CH(OH).CH_2(OH)$.

770. This tetrhydric alcohol, also termed erythro-glucin or *phycite*, occurs in *Protococcus vulgaris*, and is formed by decomposition of *erythrin* (contained in several lichens, e.g. *Rocella Montagnei*) by boiling with lime or baryta water. The lichens are best boiled with milk of lime; the excess of lime in solution is then removed by passing carbonic anhydride, the filtrate evaporated to a thin syrup and treated with alcohol. After some time erythrite crystallises out, and can be purified by recrystallisation from boiling alcohol. Orcin and orsellenic acid are found in the alcoholic mother liquors.

Erythrite forms large colourless prismatic crystals, which dissolve readily in water, difficultly in cold alcohol, and are insoluble in ether. It tastes sweet, melts at 120°, and volatilises with partial decomposition at about 300°. Potassic hydrate at 250° decomposes it into oxalic and acetic acids:

$$C_4H_6(OH)_4 + 3KOH = K_2C_2O_4 + KC_2H_3O + H_2O + 4H_2.$$

By heating with acids salts are obtained. The nitrate termed *nitro-erythrite*, $C_4H_6(O.NO_2)_4$, is formd by solution of erythrite in concentrated nitric acid, and precipitates on addition of concentrated sulphuric acid in colourless crystalline leaves. It melts at 61° and explodes violently when struck.

Hydriodic acid converts erythrite into normal secondary butylic iodide (§ 193); by long heating with hydrochloric or hydrobromic acids it exchanges two OH groups for halogen, yielding dihydrate dihaloids of its radical, which are converted into dihaloid dinitrates by a mixture of sulphuric and nitric acids.

Erythrite dichlorhydrin, $C_4H_6Cl_2(OH)_2$, forms colourless crystals readily soluble in water, alcohol, or ether, and melts at 145°.

Nitro-erythrite dichlorhydrin, $C_4H_6.Cl_2(O.NO_2)_2$, crystallises in needles, melts at 60°, and is not explosive.

Erythrite dibromhydrin, $C_4H_6Br_2(OH)_2$, melts at 130° and yields a nitrate, $C_4H_6Br_2(O.NO_2)_2$, crystallising in brilliant needles and melting at 70°.

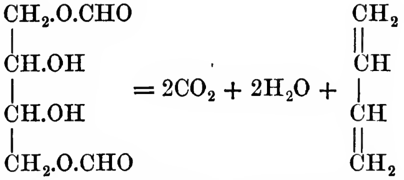
771. By heating erythrite with formic acid a monoformate is first formed, which (similarly to the decomposition of the monoformin of glycerine into allylic alcohol) decomposes between 220° and 240° into carbonic anhydride, water, and erythro-glycol:

$$C_4H_6(OH)_3(O.CHO) = CO_2 + H_2O + \underset{\text{Erythro-glycol.}}{C_4H_6(OH)_2.}$$

Erythro-glycol contains two hydrogen atoms less than butylene glycol, and probably has one of the formulæ:

$$CH_2 : CH.CH(OH).CH_2.OH \text{ or } CH_2.(OH).CH : CH.CH_2(OH).$$

It is a thick liquid, soluble in water, boiling at 199°–200°, and unites directly with two atoms of bromine. In its preparation there is also formed—without doubt from an erythrite diformate—a hydrocarbon isomeric with crotonylene, and which probably may be the isolated radical of erythrite:



$$\begin{array}{l} CH_2.O.CHO \\ | \\ CH.OH \\ | \\ CH.OH \\ | \\ CH_2.O.CHO \end{array} = 2CO_2 + 2H_2O + \begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ CH \\ \| \\ CH_2 \end{array}$$

It unites with bromine to form a tetrabromide, giving brilliant leafy crystals, melting at 115°–116°:

$$CH_2Br.CHBr.CHBr.CH_2Br\ (?).$$

Diallyl, $C_6H_{10} = CH_2 : CH.CH_2.CH_2.CH : CH_2$.

772. Diallyl is formed by treatment of allyl haloids with metals. Allylic iodide or bromide is generally used, and is heated with sodium after addition of a drop of ethylic alcohol:

$$2C_3H_5I + Na_2 = 2NaI + C_6H_{10}.$$

Finely divided silver acts in the same way at 100°. Another method consists in heating mercury allyl iodide (§ 664) with a solution of potassic cyanide:

$$2I.Hg.C_3H_5 + 2KCN = 2KI + Hg(CN)_2 + Hg + C_6H_{10}.$$

Diallyl is a colourless, mobile liquid of sp. gr. ·864, which boils at 59° and has a vapour density = 2·83. It unites with bromine to form a crystalline tetrabromide, melting at 63°, and with hydriodic acid to form the compounds $C_6H_{11}I$ and $C_6H_{12}I_2$, already mentioned (§§ 702 and 491, 2).

DERIVATIVES OF THE PENTAVALENT HYDROCARBON NUCLEUS, C_nH_{2n-3}.

DERIVATIVES OF THE RADICALS OF DISUBSTITUTED FATTY ACIDS.

773. Whilst the replacement of one hydrogen atom in the radical of a fatty acid yields compounds of the glycollic acid group only, the replacement of two hydrogen atoms can lead to several categories of bodies.

1. If the substitution occur on a single carbon atom it may occur—

a. On a terminal carbon atom. The simplest oxides must be at once aldehydes and acids.

b. On an intermediate carbon atom. There then result derivatives of the ketonic acid radicals.

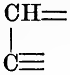
2. The substitution may occur on two different carbon atoms. There are then formed the derivatives of the double alcohol acid radicals.

If the removal of the hydrogen atoms is from neighbouring carbon atoms, double union may ensue. The acids of this kind form the acryl crotonic acid series.

Derivatives of Aldehyde Acid Radicals.

At present compounds of the nucleus $=CH.C\equiv$, ethinyl, and some aldehyde acids richer in carbon are known.

Compounds of Ethinyl,



$$\begin{array}{l} CH= \\ | \\ C\equiv \end{array}$$

774. *Halogen Compounds.*—These have been to some extent already mentioned in speaking of ethylene and acetylene.

In the first place there belongs to this group the *substitution products of acetylene*, including the metallic derivatives already mentioned (§ 752).

Ethinyl bromide, $C_2HBr = CH\vdots CBr$, or brom-acetylene, is obtained, together with acetylene, by the decomposition of bromethylene dibromide (§ 650) by boiling alcoholic potassic hydrate:

$$CH_2Br.CHBr_2 + 2KOH = 2KBr + 2H_2O + CH\vdots CBr.$$

It has not yet been prepared in the pure state, and is therefore little known; it is characterised by its spontaneous inflammability in air.

Ethinyl trichloride, trichlor ethylene, $CHCl:CCl_2$, is prepared from acetylene tetrachloride by action of alcoholic potassic hydrate, and is an oil boiling at 88°. The corresponding *ethinyl tribromide*, $CHBr:CBr_2$, is also liquid, boils at 130°, and after some time changes into a polymeric non-volatile substance.

Ethinyl pentahaloids are prepared from the foregoing by addition of chlorine and bromine, further from the tetrahaloids of glycolyl (§ 708) and acetylene (§ 752) by direct substitution :

$$CH_2Cl.CCl_3 + Cl_2 = HCl + CHCl_2.CCl_3$$
$$\text{and } CHCl_2.CH.Cl_2 + Cl_2 = HCl + CHCl_2.CCl_3.$$

Ethinyl pentachloride, trichlor ethylene dichloride, is a colourless oil of sp. gr. 1·6, which boils at 158°. *Ethinyl pentabromide* crystallises in long prisms, which melt between 48° and 50°.

Ethinyl tetrachloride ethylate is the *tetrachlor ether* obtained by direct chlorination of ether. It is liquid and boils at 189°–190° with partial decomposition.

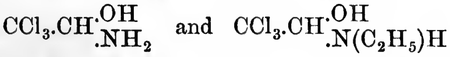
775. *Chloral*, $C_2HCl_3O = CCl_3.CHO$. This trichlor acetic aldehyde is formed by the action of chlorine on aldehyde, alcohol, sugars, and some other compounds. It is obtained most readily by passing dry chlorine into absolute alcohol to complete saturation. Considerable quantities of ethylic chloride and its chlor-substitution products volatilise with the hydrochloric acid formed according to the equation :

$$CH_3.CH_2.OH + 4Cl_2 = 5HCl + CCl_3.CHO.$$

Finally a crystalline mass remains, consisting principally of a compound of chloral with alcohol, $CCl_3.CH(OC_2H_5)(OH)$, and some chloral hydrate, $CCl_3.CH(OH)_2$, which on distillation with concentrated sulphuric acid yields pure chloral.

Chloral is a mobile, colourless liquid of penetrating odour and sp. gr. 1·502, which boils at 94·5°. On keeping it is transformed into a white, porcelain-like mass of the polymeric *parachloral*, probably trichloral, which distils at 180°, being then reconverted into ordinary chloral.

Chloral is a true aldehyde, and is therefore converted by oxidation —best with concentrated nitric acid—into trichlor acetic acid, unites with alkaline hydric sulphites to form crystalline compounds, yields, on heating with acetic anhydride to 150°, *trichlor ethylidene diacetate*, $CCl_3.CH(OC_2H_3O)_2$, a clear oil boiling at 222°; it unites directly with acetylic chloride, forming *trichlor ethylidene aceto-chloride*, $CCl_3.CHCl(O.C_2H_3O)$, which boils at 185°. With ammonia and the alkylamides it yields *hydratamides* of *trichlor ethylidene*, e.g.



$$CCl_3.CH\begin{matrix}.OH\\.NH_2\end{matrix} \quad\text{and}\quad CCl_3.CH\begin{matrix}.OH\\.N(C_2H_5)H\end{matrix}$$

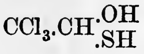
as solid, fusible masses. Phosphoric chloride converts it into ethinyl pentachloride, and nascent hydrogen in acid solution (zinc and hydrochloric acid) reconverts it into acetic aldehyde.

Chloral is distinguished from acetic aldehyde, on the one hand, by the greater energy of its union with water, and from alcohol (comp. § 384), on the other, by the more ready disruption of its carbon nucleus.

Chloral unites with water with considerable evolution of heat, forming

776. *Chloral hydrate,* $CCl_3.CH(OH)_2$, crystallising in rhombohedral forms of the monoclinic system. It melts at 46° and boils at 96°–98°. It dissolves in water to a liquid of neutral reaction and is used medicinally to produce sleep.

Chloral also unites with sulphuretted hydrogen, forming *chloral sulph-hydrate* or trichlor ethylidene hydrate thio-hydrate :



$$CCl_3.CH\begin{smallmatrix}.OH\\ .SH\end{smallmatrix}$$

crystallising in colourless prisms or leaves, melting at 77°. It boils at 123°, and is slowly decomposed by water into chloral hydrate and hydric sulphide.

Chloral hydrate, when treated with a concentrated aqueous solution of hydric sulphide, yields a crystalline mass of *chloral hydrosulphide,* $[CCl_3.CH(OH)]_2S$. This dissolves in alcohol, ether, benzene, &c., and crystallises in rhombohedric forms, melting at 127°–128° with decomposition.

Strong alcohol also unites with chloral with evolution of heat, forming '*chloral alcoholate,*' trichlor ethylidene hydrate ethylate, $CCl_2.CH\begin{smallmatrix}.OH\\ .O.C_2H_5\end{smallmatrix}$, obtained on evaporation of the solution in colourless crystals, melting at 56°. The boiling point is 114°–115°. This latter reacts with acetylic chloride, forming *chloral alcoholate acetate,* $CCl_3.CH\begin{smallmatrix}.O.C_2H_3O\\ .O.C_2H_5\end{smallmatrix}$, boiling at 198°.

Phosphoric chloride converts chloral alcoholate into tetrachlor ether :

$$CCl_3.CH(OH)(O.C_2H_5) + PCl_5 = POCl_3 + HCl$$
$$+ CCl_3.CHCl(O.C_2H_5).$$

Trichlor acetal, or trichlor ethylidene diethylate :

$$CCl_3.CH(O.C_2H_5)_2,$$

is prepared by the incomplete decomposition of ethylic alcohol by chlorine, by direct chlorination of ordinary acetal (§ 405), and by heating tetrachlor ether with alcohol :

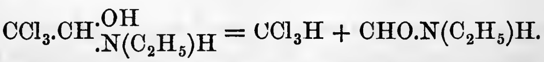
$$CCl_3.CHCl.(O.C_2H_5) + HO.C_2H_5 = CCl_3.CH(O.C_2H_5)_2 + HCl.$$

It is a colourless oil, boiling at 204°–205°.

777. Alkaline reagents decompose chloral and its derivatives into chloroform and derivatives of the formic acid radical. This decomposition is most readily effected by aqueous alkalies :

$$CCl_3.CH(OH)_2 + HOK = CCl_3H + CHO.OK + H_2O,$$

but is also effected by heating with ammonia or amines. Chloral ethylamine, e.g., thus decomposes into chloroform and ethyl formylamine :



$$CCl_3.CH\begin{smallmatrix}.OH\\ .N(C_2H_5)H\end{smallmatrix} = CCl_3H + CHO.N(C_2H_5)H.$$

778. *Bromal,* $CBr_3.CH:O$, or *tribrom-aldehyde,* is formed, similarly to chloral, when absolute alcohol is saturated with bromine, and is a colourless liquid, boiling at 172°–173°. It yields crystalline *bromal* *hydrate*, $CBr_3.CH(OH)_2$, with water, melting at 53·5°; with alcohol, *bromal alcoholate*, $CBr_3.CH(OH)(O.C_2H_5)$, melting at 44°. Both compounds are resolved into their components at 110°. The chemical properties correspond entirely with those of chloral: yields bromoform and a formate with alkalies, &c.

779. *Dichlor-acetic acid*, $C_2H_2Cl_2O_2 = CHCl_2.CO.OH$, is formed by further chlorination from monochlor acetic acid, especially when a little iodine is added and the liquid heated to boiling. It is also prepared by the action of equal molecules of chloral hydrate and potassic cyanide:

$$CCl_3.CH(OH)_2 + KCN = KCl + CHCl_2.CO.OH + HCN.$$

It is generally obtained as a liquid of extremely caustic nature, boils at 195°, and has sp. gr. 1·52 at 15°. In a state of absolute chemical purity it crystallises in rhombohedra. Its salts are mostly crystalline.

The *ethylic salt*, $CHCl_2.CO.O.C_2H_5$, is obtained by saturation of its alcoholic solution with hydrochloric acid, as also by the action of sodic ethylate on tetrachlor ethylene:

$$CCl_2 : CCl_2 + 2NaO.C_2H_5 = 2NaCl + C_2H_4 + CHCl_2.CO.O.C_2H_5,$$

and by action of chloral hydrate on an alcoholic solution of potassic cyanide. It is a colourless oil, boiling at 153°–156°.

Dichlor acetamide, $CHCl_2.CO.NH_2$, prepared from ethylic dichlor acetate and ammonia, crystallises in difficultly soluble prisms, melting at 94·5°. It boils without decomposition at 233°–234°.

Dibrom-acetic acid, $C_2H_2Br_2O_2 = CHBr_2.CO.OH$, is readily obtained by saturating boiling monobrom-acetic acid with bromine vapour with exposure to sunlight, and by heating acetic acid with two molecules of bromine in sealed tubes to 130°. It is crystalline, melts between 45° and 50°, and boils somewhat above 230°. Sp. gr. 2·25.

On heating brom-acetylic bromide with a molecule of bromine to 150°, *dibrom-acetylic bromide*, $CHBr_2.COBr$, is formed, boiling at 194°, and when treated with alcohol yielding *ethylic dibrom-acetate*, $CHBr_2.CO.O.C_2H_5$, boiling at 194°.

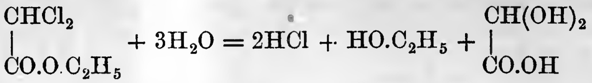
Diiod-acetic acid, $CHI_2.CO.OH$, is prepared from dibrom-acetic acid in like manner to moniod-acetic acid from monobrom-acetic acid (§ 711). Ethylic diiod-acetate, first formed, is a yellowish oil, which is saponified by milk of lime and a concentrated solution of the resulting calcic salt, decomposed by hydrochloric acid. Diiod-acetic acid crystallises in sulphur-yellow rhombohedra, which are difficultly soluble in water, and decompose on heating with evolution of iodine. Its salts are crystalline, the lead and silver salts difficultly soluble. The latter explodes on heating.

780. *Brom-glycollic acid*, $CHBr(OH).CO.OH$, is formed by heating argentic dibrom-acetate with water:

$$CHBr_2.CO.OAg + HOH = AgBr + CHBr(OH).CO.OH,$$

and by similar treatment of its silver salts yields glyoxalic acid.

781. *Glyoxylic acid, glyoxalic acid*, $C_2H_2O_3 = CHO.CO.OH$ or $C_2H_4O_4 = CH(OH)_2.CO.OH$, a true aldehyde acid, is formed, in addition to the above-mentioned method, from the dihalogen substituted ethylic acetates by heating with water to 120°:

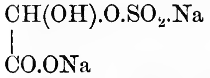


$$\begin{array}{l}CHCl_2\\|\\CO.O.C_2H_5\end{array} + 3H_2O = 2HCl + HO.C_2H_5 + \begin{array}{l}CH(OH)_2\\|\\CO.OH\end{array}$$

and, together with glycollic acid, glyoxal, and oxalic acids, by the oxidation of ethylic alcohol or ethylene glycol by nitric acid. As formerly mentioned (§ 712), it can be obtained pure by repeated crystallisation of its difficultly soluble calcic salt. By addition of the requisite quantity of oxalic acid the free acid is obtained in solution, and is left on evaporation of the filtrate as a faint yellow, readily soluble syrup. It volatilises unchanged in water vapour.

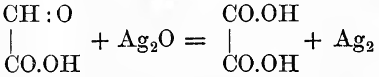
Its salts are crystalline, and when dried at 100° possess the formula $CH(OH)_2.CO.OM$. The calcic salt, $[CH(OH_2).CO.O]_2Ca$, is very difficultly soluble in cold water, and loses no water at 100°. The ammonic salt, on the other hand, appears to have the formula $CHO.CO.ONH_4$.

The aldehyde properties of the acid are shown in many ways. Its alkali salts unite with alkaline hydric sulphites to form crystalline compounds:



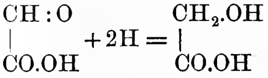
$$\begin{array}{l}CH(OH).O.SO_2.Na\\|\\CO.ONa\end{array}$$

Argentic oxide is reduced both by the free acid and its salts, oxalic acid being formed:



$$\begin{array}{l}CH:O\\|\\CO.OH\end{array} + Ag_2O = \begin{array}{l}CO.OH\\|\\CO.OH\end{array} + Ag_2$$

Nascent hydrogen converts it into glycollic acid, a body which stands to it in the relation of a primary alcohol:



$$\begin{array}{l}CH:O\\|\\CO.OH\end{array} + 2H = \begin{array}{l}CH_2.OH\\|\\CO.OH\end{array}$$

Both actions are combined when glyoxylates are heated with strong bases. If lime water be added to a solution of calcic glyoxylate a white precipitate is first produced, which—freshly produced—is readily soluble in acetic acid and is a basic calcic glyoxylate. After some time, or more quickly on boiling, it decomposes into soluble glycollate and insoluble oxalate (equation § 712).

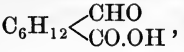
Dieth-oxyglyoxylic acid, $CH(O.C_2H_5)_2.CO.OH$, is obtained as a sodic salt by the decomposition of ethylic dichlor-acetate with three molecules of sodic ethylate:

$$CHCl_2.CO.OC_2H_5 + 3NaO.C_2H_5 = 2NaCl + CH(OC_2H_5)_2CO.ONa + (C_2H_5)_2O.$$

On heating with ethylic iodide it yields *ethylic diethyl glyoxylate*, $CH(O.C_2H_5)_2.CO.O.C_2H_5$, a colourless oil, boiling at 199°, of sp. gr. ·994 at 18°, and which reacts readily with ammonia, forming *diethyl glyoxyl-amide*, $CH(O.C_2H_5)_2.CO.NH_2$. This latter crystallises in nacreous rhombic tables, melting at 76·5° and subliming slowly at 100°.

782. Some members richer in carbon are known of the aldehyde acids. *Succinaldehydic acid*, $CHO.CH_2.CH_2.CO.OH$, is formed by incomplete oxidation of succinic aldehyde (§ 756), and is still little known.

The acids of the series $C_{n'}H_{2n'-3}.CO.OH$ (see derivatives of the radicals C_nH_{2n-5}), on oxidation with nitric acid, yield, with halving of their nuclei, first aldehyde acids, which further oxidise to dibasic acids of the series $C_nH_{2n}(CO.OH)_2$. There have been so obtained

Subero-aldehydic acid, $C_8H_{14}O_3$ =  $C_6H_{12}{<}\begin{matrix}CHO\\CO.OH\end{matrix}$, from palmitolic acid.

Azelo-aldehydic acid, $C_9H_{16}O_3$, from stearolic acid.

Brassylo-aldehydic acid, $C_{11}H_{20}O_3$, from behenolic acid.

All three are oils which can be distilled unchanged with water vapour. Subero-aldehydic acid can be distilled alone without considerable decomposition; its boiling point is about 202°.

Derivatives of the Ketonic Acid Radicals.

783. The substances belonging to this group are almost entirely derived from the ethereal salts of those ketonic acids which contain the CO group combined by means of one carbon atom with the carboxyl group CO.OH.

These ethereal salts are constituted on the general formula:

$$CH_3.CO.CXY.CO.OC_2H_5,$$

in which X and Y may be either hydrogen atoms or alcohol radicals, C_nH_{2n+1}, &c.

784. Among the tricarbonide compounds of this group may be classed *a-dibrom-propionic acid*, $CH_3.CBr_2.CO.OH$. This body results from brom-propionic acid by heating with two molecules of bromine in a sealed tube. It forms a colourless crystalline mass melting at 62° and boiling at 220°–221°, with slight decomposition. Zinc and sulphuric acid reduce it to propionic acid. The *barium salt*, $(CH_3.CBr_2.CO.O)_2Ba + 9OH_2$, crystallises in silky needles, which lose all their water at 90°, and also gradually on exposure to air. The *ethylic salt*, $CH_3.CBr_2.CO.O.C_2H_5$, boils at 190° (comp. the isomeric β-dibrom-propionic acid, § 793).

785. As already mentioned (§ 559, 4), metallic sodium acts upon ethylic acetate with formation of sodium ethylate and ethylic sodaceto-acetate, probably as shown by the equation:

$$3CH_3.CO.O.C_2H_5 + 2Na_2 = 3NaOC_2H_5 \\ + CH_3.CO.CHNa.CO.O.C_2H_5,$$

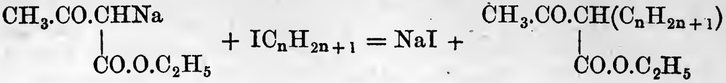
this latter body serving as the starting point for all the members of the group, since by treatment with an acid ethylic aceto-acetate, $CH_3.CO.CH_2.CO.O.C_2H_5$, is obtained.

This body can exchange one of the hydrogen atoms of the *methene* group (CH_2), combined to the two CO groups, for sodium, when brought in contact with the metal or with dry sodic ethylate:

$$2CH_3.CO.CH_2.CO.O.C_2H_5 + Na_2 = 2CH_3.CO.CHNa.CO.O.C_2H_5 \\ + H_2.$$

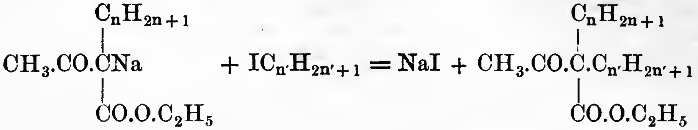
This sodium compound reacts readily with the haloid compounds of organic radicals, the sodium being replaced by the alcohol radical, &c.

In the case of the haloid compounds of the ordinary alcohol radicals the homologues of ethylic aceto-acetate are produced:



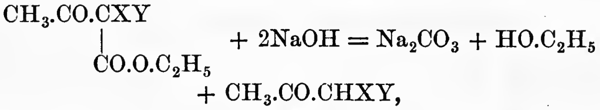
$$\begin{array}{l}CH_3.CO.CHNa\\ \quad |\\ \quad CO.O.C_2H_5\end{array} + IC_nH_{2n+1} = NaI + \begin{array}{l}CH_3.CO.CH(C_nH_{2n+1})\\ \quad |\\ \quad CO.O.C_2H_5\end{array}$$

In these mono-substituted bodies the remaining H atom at this same carbon may also be replaced by sodium, forming *ethylic sod-alkyl aceto-acetates*, which again react with the alcoholic haloid compounds, giving dialkyl aceto-acetic ethers:



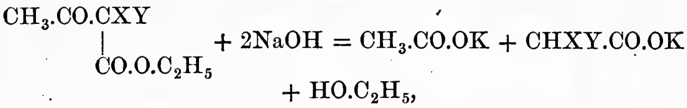
$$\begin{array}{l}\qquad\qquad C_nH_{2n+1}\\ \qquad\qquad |\\ CH_3.CO.CNa\\ \qquad\qquad |\\ \qquad\qquad CO.O.C_2H_5\end{array} + IC_{n'}H_{2n'+1} = NaI + \begin{array}{l}\qquad\qquad C_nH_{2n+1}\\ \qquad\qquad |\\ CH_3.CO.C.C_{n'}H_{2n'+1}\\ \qquad\qquad |\\ \qquad\qquad CO.O.C_2H_5\end{array}$$

On saponification with alkalies the ethylic aceto-acetates, whether simple or compound, split up in two ways, either into a carbonate and a ketone:



$$\begin{array}{l}CH_3.CO.CXY\\ \qquad |\\ \qquad CO.O.C_2H_5\end{array} + 2NaOH = Na_2CO_3 + HO.C_2H_5 + CH_3.CO.CHXY,$$

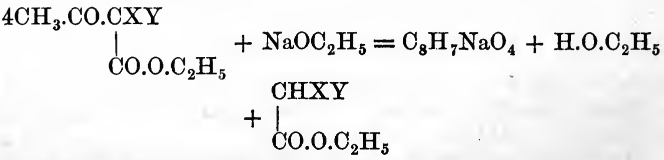
or into acetic acid and a substituted acetic acid:



$$\begin{array}{l}CH_3.CO.CXY\\ \qquad |\\ \qquad CO.O.C_2H_5\end{array} + 2NaOH = CH_3.CO.OK + CHXY.CO.OK + HO.C_2H_5,$$

depending on the concentration of the alkali used. By using dilute solutions the first-mentioned products predominate; with increased strength of the alkaline solution, the latter, the quantitative relations of the two depending, however, to some extent on the nature of the substituting radical in the ethereal salt.

By heating ethereal salts of ketonic acids with dry sodium ethylate, large quantities of ethereal salts of the form $CHXY.CO.O.C_2H_5$ are produced, probably also with polymers of the group $CH_2.CO$. The reaction appears to be:



$$4\begin{array}{l}CH_3.CO.CXY\\ \qquad |\\ \qquad CO.O.C_2H_5\end{array} + NaOC_2H_5 = C_8H_7NaO_4 + H.O.C_2H_5 + \begin{array}{l}CHXY\\ |\\ CO.O.C_2H_5\end{array}$$

The ketonic acid molecules are therefore somewhat unstable, like all organic bodies containing many oxygen atoms in neighbouring combination, the nucleus easily splitting up, and in consequence they constitute very important intermediate bodies, or stages, for the synthesis of ketones and organic acids and their derivatives.

786. *Ethylic aceto-acetate,* $CH_3.CO.CH_2.CO.O.C_2H_5$. The best method of preparing this body is by acting on 1,000 grms. of pure and perfectly dry ethylic acetate with 100 grms. of sodium cut in small pieces of about $\frac{1}{4}$ inch cube. The acetic ether should be contained in a very capacious flask connected with an inverted condenser. The sodium is introduced all at once, the first violent action slightly moderated by immersing the flask in cold water. Afterwards it must be heated gently on a water bath, being constantly shaken the while, until all the sodium has disappeared. It is advantageous to add about 200 cc. of dry benzene to the ether, to moderate the first action. After all the sodium has dissolved 550 grms. of 50 % acetic acid is added to the still warm product, which is then allowed to cool, when about $\frac{1}{4}$ litre of water is added. and the whole distilled in a water bath to get rid of the excess of ethylic acetate. The residue is now treated with sufficient water to dissolve the sodic acetate, and the oily layer which rises to the surface separated and distilled. After one or two fractional distillations a fraction between 175° and 185° will be obtained, and may be used for most purposes. The pure body boils between 181° and 183°, a small quantity decomposing at each distillation. A portion boiling above 200° solidifies on cooling to a crystalline mass of *dehydracetic acid*, $C_8H_8O_4$.

The same body is formed on heating ethylic aceto-acetate in a sealed tube at 200°–230° along with ethylic acetate:

$$4CH_3.CO.CH_2.CO.OC_2H_5 = C_8H_8O_4 + 4CH_3.CO.O.C_2H_5.$$

It is a difficultly soluble acid, forming needles, melting at 108°.

Ethylic aceto-acetate is a liquid of a pleasant fruity odour, of sp. gr. 1·03 at 5°, boiling at 180·8° (corr.) It reddens litums in presence of water, and gives a beautiful dark violet coloration with ferric chloride. It distils unchanged in a current of steam. Strong acids, also water at 150°, split it up into acetone, alcohol, and carbonic acid. Alkalies act similarly; when concentrated, however, giving more or less acetic acid.

Nascent hydrogen gives β-oxybutyric acid:

$$CH_3.CO.CH_2.CO.O.C_2H_5 + Na_2 + 2H_2O$$
$$= CH_3.CH(OH).CH_2.CO.ONa + HO.C_2H_5 + NaOH.$$

Dilute permanganate solution oxidises it to oxalic and acetic acids.

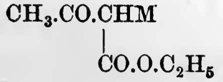
Bromine forms an addition product, $C_6H_{10}O_3Br_2$, and also a substitution product, $C_6H_8Br_2O_3Br_2$. Chlorine gives

$$CH_3.CO.CCl_2.CO.O.C_2H_5,$$

boiling at 205°–207°, sp. gr. 1·293 at 16°.

Phosphoric chloride gives two isomeric monochlor crotonic acids, $C_4H_5ClO_2$.

By the action of strong bases one hydrogen atom in ethylic aceto-acetate may be replaced by a metal, thus producing metallic derivatives of the form



$$\begin{array}{l} CH_3.CO.CHM \\ \qquad\qquad\quad | \\ \qquad\qquad\quad CO.O.C_2H_5 \end{array}$$

In the case of the alkali metals, e.g. sodium, the metal may be allowed to act directly on the ethylic aceto-acetate in benzene solution.

On distilling away the liquid in vacuo the sodium compound is left as a beautiful white, silky, crystalline mass.

A better plan is to precipitate the sodium compound by the addition of a very small quantity of water. It may then be rapidly filtered and dried by pressure.

Other Metallic Derivatives.

Ethylic aluminum aceto-acetate, $(C_6H_9O_3)_3.Al$, separates, on mixing ethylic aceto-acetate and an alkaline solution of an aluminum salt, in the form of beautiful shining needles, melting at 76°, soluble in ether, benzene, and CS_2, and distilling undecomposed under slightly diminished pressure.

The *copper* compound $(C_6H_9O_3)_2.Cu$, easily obtained by shaking ethylic aceto-acetate with ammoniacal copper solution, is a green crystalline powder insoluble in water, but dissolving readily in hot benzene, alcohol, carbon disulphide, ethylic iodide, brom-benzol, and other oily liquids, from which it crystallises on cooling in brilliant green needles.

If carefully heated to 178° it sublimes unchanged, melts at 182°, and decomposes at a higher temperature. Mercury, cobalt, barium, magnesium, &c., form similar compounds.

Ethylic nitroso-aceto-acetate, $CH_3.CO.CH(NO).CO.O.C_2H_5$, is produced when one molecule of ethylic aceto-acetate in dilute alkaline solution is treated with an equivalent of potassic nitrite and the mixture acidified with dilute sulphuric acid.

After shaking out with ether, the nitroso compound is obtained as a yellow oil, which solidifies after some time. It may be crystallised from chloroform, and then forms large centimetre-thick, colourless, shining prisms, melting at 52°–54°. It is totally decomposed on distillation. It gives an orange-red reaction with phenol and sulphuric acid.

Chloroform acts violently on ethylic sod-aceto-acetate with formation of oxyuvtic acid.

Carbonic sulphide also acts on the sodium compound, giving a sulpho-acid, thio-rufic acid, $C_{10}H_{14}S_3O_4$, which forms with sodium and calcium very characteristic brilliant red crystalline salts. By the simultaneous action of carbonic sulphide and plumbic or zincic oxide on ethylic aceto-acetate

Ethylic thiocarb-aceto-acetate, $CH_3.CO.C(CS).CO.O.C_2H_5$, is produced. It is a straw-yellow crystalline body, melting between 156° and 160°.

Sodium amalgam reduces it to *a-methyl β-oxybutyric acid*, a yellow syrup which quickly changes into an ethereal anhydride, and by heating alone or with hydriodic acid is converted into α-methyl crotonic acid.

Ethylic methyl aceto-acetate gives with phosphoric chloride, monochlor methyl crotonic acid, $CH_3.CCl:C.CH_3.CO.OH$, which splits up under the influence of alkalies into monochlor butylene and carbonic acid.

When acted upon by nitrous acid, ethylic methyl aceto-acetate gives nitroso-methyl acetone, $CH_3.CO.CH(NO).CH_3$, or nitroso-propionic acid, $CH_3.CH(NO).CO.OH$, according to the strength of the acid employed.

The former body crystallises from chloroform in white prisms of a peculiar sweet odour, melts at 74°, boils undecomposed at 185°–186°. It gives with phenol and sulphuric acid a bright red coloration.

The latter body results when methyl aceto-acetic ether in dilute alkaline solution is treated with nitrous acid. Ethylic nitroso-propionate is thus produced in brilliant prismatic needles, melting at 94° and boiling with slight decomposition at 233°. The free acid is obtained by saponification. It gives no colour reaction with phenol and sulphuric acid.

787. By the action of methylic iodide on ethylic sod-aceto-acetate *Ethylic methyl aceto-acetate*, $CH_3.CO.CH(CH_3).CO.O.C_2H_5$, is produced. It is a liquid very similar to the original body, boils at 186°–187°, and has a sp. gr. of 1·009 at 12°.

It decomposes with alkalies into carbonate, ethylic alcohol, and methyl-ethyl ketone (§ 449). By heating with sodium ethylate ethylic propionate is formed in quantity. It dissolves one atom of sodium and forms $CH_3.CO.C(CH_3)Na.CO.O.C_2H_5$, which gives, on treatment with methyl iodide, *ethylic dimethyl aceto-acetate:*

$$CH_3.CO.C(CH_3)_2.CO.O.C_2H_5,$$

a liquid almost insoluble in water, boiling at 190°, and of sp. gr. ·9913 at 16°.

Phosphoric chloride gives *monochlor dimethyl crotonic acid*, $CH_2.CCl.C(CH_3)_2.CO.OH$, forming monoclinic crystals melting at 63°.

Many other substituted ethers have been obtained in a similar manner.

Ethylic ethyl aceto-acetate, $CH_3.CO.CH(C_2H_5).CO.O.C_2H_5$, boils at 195°, sp. gr. ·998 at 16°, gives methyl-propyl ketone on saponification with alkalies; with sodium ethylate it yields ethylic butyrate.

Ethylic diethyl aceto-acetate, $CH_3.CO.C(C_2H_5)_2.CO.O.C_2H_5$, boils at 210°–212°.

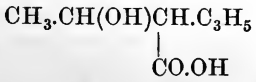
Nascent hydrogen reduces it to diethyl β-oxybutyric acid:

$$CH_3.CH(OH).C(C_2H_5).CO.OH.$$

Ethylic allyl aceto-acetate, prepared by the action of allylic iodide on the sodium compound of the ether, is a liquid boiling at 205°–206°, sp. gr. ·982 at 20°.

Baric hydrate splits it up into metacetone, mesitylenic oxide, and an isomeric *allyl acetone*, $CH_3.CO.CH_2.C_3H_5$, a colourless liquid, boiling at 130° and not combining with hydric sodic sulphite. It gives, on oxidation, allyl acetic acid, $C_3H_5.CH_2.CO.OH$, a liquid boiling at 182°.

Sodium amalgam reduces ethylic allyl aceto-acetate to *a-allyl β-oxybutyric acid:*

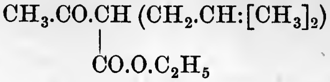


$$\begin{array}{l}CH_3.CH(OH)CH.C_3H_5\\ \qquad\qquad\qquad\quad |\\ \qquad\qquad\qquad\; CO.OH\end{array}$$

Ethylic diallyl aceto-acetate, $CH_3.CO.C(C_3H_5)_2.CO.O.C_2H_5$, is a liquid boiling at 239°–241°, of sp. gr. ·948 at 25°. It yields diallyl acetone and diallyl acetic acid on saponification.

Ethylic isopropyl aceto-acetate, $C_9H_{16}O_3$, is a colourless liquid having the odour of wet straw; it boils at 201°, and gives isobutyl methyl ketone, $CH_3.CO.CH_2.CH.(CH_3)_2$, on saponification.

Ethylic isobutyl aceto-acetate:



$$\begin{array}{l} CH_3.CO.CH\ (CH_2.CH{:}[CH_3]_2) \\ \quad\quad\quad\ | \\ \quad\quad\quad CO.O.C_2H_5 \end{array}$$

is an oily body, boiling at 217°–218°.

Ethylic diisobutyl aceto-acetate, $C_{14}H_{26}O_3$, boils at 250°–253°.

Ethylic cetyl aceto-acetate, $CH_3.CO.CH(C_{16}H_{33})CO.O.C_2H_5$, a liquid which does not distil undecomposed. It yields cetyl acetic acid and cetyl-methyl ketone on saponification.

The corresponding ethylic heptyl and octyl aceto-acetates have also been prepared, and from them the respective substituted acetic acids and ketones (comp. §§ 596, 454*a*, and 455*c*).

788. *Aceto-propionic acid*, $CH_3.CO.CH_2.CH_2.CO.OH$, is obtained as baric salt by the action of baric hydrate on ethylic aceto-succinate (§ 913).

788*a*. *Dehydracetic acid*, $C_8H_8O_4$. The exact constitution of this body is not yet known. It is a constant product of the decomposition of ethylic aceto-acetate by heat, being formed especially when the vapour of that body is passed through a red-hot tube.

It forms tabular rhombic crystals, melting at 108·6°, boils at 269° with carbonisation, and dissolves in 1,000 pts. OH_2 at 6°. It may be crystallised from concentrated hydrochloric or nitric acids, and resists the action of strong sulphuric acid. On the other hand, it is most easily acted upon by alkalies, splitting up into acetone, acetic and carbonic acids. It yields chlorine and bromine substitution bodies.

Bodies corresponding to ethylic aceto-acetate and many of its derivatives have been obtained from methylic, propylic, amylic, &c., acetates by the action of metallic sodium.

Derivatives of the Double Alcohol Acid Radicals.

789. In the fatty acid radicals two hydrogen atoms in combination with different carbon atoms can be eliminated, and replaced either by other radicals or when the carbon atoms are contiguous by double union of the latter. In this manner two series of acids result—namely, the double alcoholic acids or dioxy-acids and the unsaturated monobasic acids of the acryl olefine series.

Unsaturated Monobasic Acids of the Formula

$$C_nH_{2n-3}O.OH = C_{n'}H_{2n'-1}.CO.OH.$$

790. The acids of this series differ from the fatty acids containing the same number of carbon atoms by a deficiency of two hydrogen atoms, whereby two neighbouring carbon atoms of the group $C_{n'}H_{2n'-1}$ are connected by double linking. In consequence of this they combine the properties of monobasic acids with those of hydrocarbons of the olefine series. As representing the first they form salts, &c., fully analogous in their properties to those of the fatty acids.

On the other hand they are enabled, owing to the double union of the carbon, to combine directly with the halogens or other elements, the divalent combination being resolved into monovalent. The double carbon union gives rise, further, to another peculiarity—namely, the splitting up by action of fused potassic hydrate into two fatty acid molecules, the sum of the carbon atoms in which is equal to that of the original acid :

$$C_nH_{2n-3}O.OH + 2KOH = C_{n'}H_{2n'-1}O.OK \\ + C_{(n-n')}H_{2(n-n')-1}O.OK + H_2.$$

Since unsaturated organic compounds are most easily oxidised in the places where double carbon combination or bonds exist, and the splitting up of the nucleus being a consequence of oxidation, the position of the double combination can in many cases be determined by this method; at the same time it is not one of general applicability.

For example, the two normal isomeric crotonic acids :

$$(\alpha)\ CH_3.CH : CH.CO.OH \text{ and } (\beta)\ CH_2 : CH.CH_2.CO.OH,$$

both give, when melted with OKH, two molecules of potassic acetate, a result to be expected from the formula of the α-acid, whereas the β should yield formic and propionic acids. The cause of this apparently striking divergence from theory is accounted for by the observed fact that β-crotonic acid is converted by simply heating to 180° directly into the α-acid :

$$CH_2 : CH.CH_2.CO.OH = CH_3.CH : CH.CO.OH,$$

so that really only the α-acid is subjected to the action of the melting alkali.

791. The higher members of the series are termed oleic acids, and occur in fatty liquid oils as glycerine salts along with salts of the fatty acids, from which they may be separated by the solubility of their lead salts in ether, as already stated (§ 563).

The lower members of the series combine with hydrogen to form acids of the form $C_nH_{2n-1}O.OH$; the higher members, however, do not possess this power.

The halogen addition products are decomposed by alcoholic potash in the same way as the alkylene dibromides; that is, with every bromine atom a hydrogen atom is split off, so that at first simple halogen substitutes of the original acid result, and finally halogen free acids with less hydrogen of the formula $C_nH_{2n-3}.CO.OH$:

$$C_nH_{2n-2}Br.CO.OK + KOH = KBr + H_2O + C_nH_{2n-3}CO.OK.$$

Several of the higher members of this series are changed by contact with nitrous acid into isomers (difficultly fusible), the construction of which is not yet fully known.

Acrylic Acid, $C_3H_4O_2 = CH_2 : CH.CO.OH$.

792. This acid is obtained by the oxidation of an aqueous solution of acroleïn (§ 763) by means of freshly prepared argentic oxide. The action completes itself after some time at the ordinary temperature, when the whole is heated to boiling and the dissolved argentic acrylate decomposed by sodic hydrate, the sodic salt evaporated to dryness and decomposed by dilute sulphuric acid and the acrylic acid separated by distillation.

Glycerin iodo-propionic acid, when treated with alcoholic potash, gives along with a salt of hydracrylic also that of acrylic acid. A better method consists in distilling glycerine iodo-propionic acid over finely powdered plumbic oxide; the hydracrylic acid is then decomposed into water and acrylic acid.

In the dry condition acrylic acid is only obtained by decomposing a silver or lead salt by dry SH_2, in which case it is a colourless, strongly acid liquid, crystallising in the cold and miscible in all proportions with water. It melts between 7° and 8° and boils at 139°–140°. It combines very slowly with nascent hydrogen, but by long contact with zinc and dilute sulphuric acid in the warm it is completely converted to propionic acid:

$$CH_2 : CH.CO.OH + 2H = CH_3.CH_2.CO.OH.$$

Most of its salts are easily soluble in water. Its sodium salt can be obtained by evaporation as a white, scarcely crystalline mass, not dissolving to any appreciable extent even in boiling alcohol. The lead salt forms long shiny prisms of the formula $(C_3H_3O_2)_2Pb$. The silver salt, $C_3H_3O_2Ag$, crystallises in fine needles.

The potassic salt, when fused with potash, gives potassic acetate and formate:

$$C_3H_3O.OK + KOH + OH_2 = C_2H_3O.OK + CHKO_2 + H_2.$$

Ethylic acrylate is the only ethereal salt of acrylic acid known, being obtained from β-dibrom-propionic ether by the action of zinc and sulphuric acid:

$$CH_2Br.CHBr.CO.OC_2H_5 + H_2 = 2HBr + CH_2 : CH.CO.OC_2H_5.$$

It is a liquid of penetrating odour, boiling at 101°–102°, of sp. gr. at 0° ·925.

793. The haloid acids combine with acrylic acid to form the so-called β-halogen propionic acids (§ 744), by means of which it can easily be reconverted into hydracrylic acid. The halogens combine similarly, bromine forming β-dibrom-propionic acid, isomeric with α-dibrom-propionic acid (§ 784).

β-Dibrom-propionic acid, $CH_2Br.CHBr.CO.OH$, also obtained by the oxidation of allyl alcohol dibromide with strong nitric acid; it is colourless and crystalline, melts at 64°–65°, dissolves easily in water, and decomposes on distillation. Its ethylic salt is a fruity-smelling oil, boiling between 211° and 214°.

Boiling alcoholic potash converts it into the potassium salt of

β-Brom-acrylic acid, $CHBr : CH.CO.OH$, which latter crystallises in small prisms, fusing between 69° and 70°, and combining directly with hydric bromide to reform β-dibrom-propionic acid. The potassium salt forms beautiful tables.

β-Brom-acrylic acid, $CH_2 : CBr.CO.OH$, obtained with difficulty from α-dibrom-propionic acid by treatment by alcoholic potash, also melts at 69°–70°. The potassic salt forms rhombic tables.

It combines likewise with hydric bromide to form β-dibrom-propionic acid, so that by this means propionic can be reduced to acrylic acid.

Crotonic Acids, $C_4H_6O_2$.

794. Three isomeric acids of this formula are known.

1. *α-Crotonic acid*, $CH_3.CH:CH.CO.OH$, improperly termed *crotonic acid*, is obtained by the oxidation of its aldehyde (§ 765), by dry distillation of β-oxybutyric acid (§ 747, 2):

$$CH_3.CH(OH).CH_2.CO.OH = H_2O + CH_3.CH:CH.CO.OH,$$

by heating ethylic α-brom-butyrate with potassic hydrate:

$$CH_3.CH_2.CHBr.CO.O.C_2H_5 + 2OKH = KBr + OH_2 + HO.C_2H_5 \\ + CH_3.CH:CH.CO.OK,$$

and by boiling allylic cyanide with potash.

In the latter case, however, a shifting of the hydrogen atoms and the position of the double carbon union takes place. The structural constitution of allylic iodide is undoubtedly $CH_2:CH.CH_2I$. This on heating with potassic cyanide should give the nitrile of β-crotonic acid, $CH_2:CH.CH_2.CN$, which by treatment with potassic hydrate would be expected to yield β-crotonic acid, instead of which α-crotonic acid is formed.

Owing to the easy convertibility of the β-acid to the α, the facts are not very surprising; indeed, it is quite a question whether the nitrile contains the nucleus of the α-acid and reacts in this manner:

$$CH_2:CH.CH_2I + KCN = KI + CH_3.CH:CH.CN,$$

or if the nitrile of the β-acid is first formed, and during the replacement of the nitrogen atom by oxygen the hydrocarbon radical changed to that of the α-crotonic acid.

α-Crotonic acid crystallises in tables or needles melting at 72°, and distils at 180° without change; it is slowly converted by nascent hydrogen into butyric acid; nitric acid oxidises it to acetic and oxalic acids, chromic acid to acetic and carbonic acids, and by melting with potassic hydrate it is split up into two acetic acid molecules.

Hydric iodide and bromide combine with it to form the two possible α- and β halogen butyric acids:

$$aCH_3.CH:CH.CO.OH + aHI = bCH_3.CH_2.CHI.CO.OH \\ + (a - b)CH_3.CHI.CH_2.CO.OH,$$

which by boiling with potash yield a mixture of α- and β-oxybutyric acids.

795. Two molecules of phosphoric chloride act with great energy on one molecule of ethylic aceto-acetate, forming a mixture of the chlorides of two different crotonic acids.

Similarly to the reaction between phosphoric chloride and acetone (§ 445), the action is here not exactly confined to that represented in the equation:

$$CH_3.CO.CH_2.CO.O.C_2H_5 + 2PCl_5 = 2POCl_3 + C_2H_5Cl \\ + CH_3.CCl_2.CH_2.CO.Cl;$$

but hydric chloride is also formed under the assumption of difference in 'place value' of the hydrogen atom:

$$aCH_3.CCl_2.CH_2.CO.Cl = aHCl + bCH_3.CCl:CH.CO.Cl \\ + (a - b)CH_2:CCl.CH_2.CO.Cl.$$

On contact with water the chlorides decompose into the two isomeric chlor-crotonic acids:

$$CH_3.CCl.CH.CO.OH \text{ and } CH_2:CCl.CH_2.CO.OH,$$

which are separable by difference of solubility.

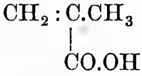
Chlor α-crotonic acid, $CH_3.CCl:CH.CO.OH$, crystallises in colourless prisms, melting at 94°, boiling 206°–211°, soluble in 35 parts cold water, easily in hot water. Sodium amalgam gives α-crotonic acid:

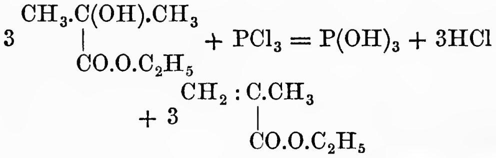
$$CH_3.CCl:CH.CO.OH + Na_2 = NaCl + CH_3.CH:CH.CO.ONa.$$

Probably the same crotonic acid results from the action of zinc and HCl on *trichlor crotonic acid,* $C_4H_3Cl_3O_2$, obtained by the oxidation of trichlor crotonic aldehyde with nitric acid in colourless needles, melting at 44°.

Chlor β-crotonic acid, $CH_2:CCl.CH_2.CO.OH$, forms needles difficultly soluble in water, melting at 59·5°, and subliming even at ordinary temperatures and boiling at 195°. Sodium amalgam in aqueous solution gives the salt of

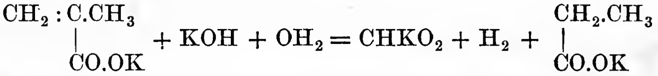
796. 2. *β-Crotonic acid,* $CH_2:CH.CH_2.CO.OH$, *isocrotonic* or *quartenylic acid,* a liquid not freezing at −15°, boiling at 172°, but leaving a small residue of α-crotonic acid at each distillation and completely changed into the latter by heating in tube to 180°. β-Crotonic acid, by heating with potassic hydrate, splits up into acetic acid only, whereas from its structure formic and propionic acids were to be expected.

3. *Meth-acrylic acid,*  $\begin{array}{c} CH_2:C.CH_3 \\ | \\ CO.OH \end{array}$, results in the form of its ethylic salt from the action of PCl_3 on the ethylic salt of α-hydroxy-isobutyric acid (§ 747, 3):



$$3\begin{array}{c} CH_3.C(OH).CH_3 \\ | \\ CO.O.C_2H_5 \end{array} + PCl_3 = P(OH)_3 + 3HCl + 3\begin{array}{c} CH_2:C.CH_3 \\ | \\ CO.O.C_2H_5 \end{array}$$

The free acid is liquid at 0°, and is broken up by fused potassic hydrate into formic and propionic acids:



$$\begin{array}{c} CH_2:C.CH_3 \\ | \\ CO.OK \end{array} + KOH + OH_2 = CHKO_2 + H_2 + \begin{array}{c} CH_2.CH_3 \\ | \\ CO.OK \end{array}$$

A brom substitution product, brom-meth-acrylic acid, results from heating citraconic dibromide with aqueous alkalies (see citra-dibrom-pyrotartaric acid).

Acids of the Formula $C_5H_8O_2$.

Four of these acids are known.

797. 1. *Methyl crotonic acid,* $CH_3.CH:C(CH_3).CO.OH$, *tiglic acid,* or *α-β-dimethyl acrylic acid.* By action of phosphorus chloride on ethylic eth-meth-oxalate (comp. § 749, 2) *ethylic methyl crotonate*, $CH_3.CH : C(CH_3).CO.O.C_2H_5$, is obtained as a liquid boiling at 156°. The free acid crystallises in triclinic prisms, melting at 62°, and is decomposed into acetate and propionate by fusion with potassic hydrate.

Croton oil (from the seeds of *Croton Tiglium*) contains, in addition to the glycerine salts of numerous acids of the acetic series, the salt of an acid, *tiglic acid*, which appears to be identical with methyl crotonic acid; it melts at 64° and boils at 198·5°. This acid is also obtained from oil of camomile (*Anthemis nobilis*), by saponification of the alkaloids of *Veratrum Sabadilla* and by heating angelic acid. Hydrobromic acid converts it into a brom-valeric acid.

2. *β-Dimeth-acrylic acid*, $(CH_3)_2C : CH.CO.OH$, is prepared from hydroxy-isopropyl acetic acid, $(CH_3)_2.C(OH).CH_2.CO.OH$, by distillation with sulphuric acid. It forms monoclinic prisms, melting at 70°.

3. *Angelic acid* occurs in the root of *Angelica archangelica* and in *Eurysangium sumbul*, camomile oil and the roots of various Umbelliferæ, from which it may be obtained by boiling the roots with milk of lime and decomposing the filtered solution with sulphuric acid, and distilling in a current of steam, the angelic acid passing over, and from laserpitin and peucedanin by the action of potassic hydrate.

The acid forms large monoclinic prisms, melting at 45° and boiling at 185°, a portion being converted into an isomeric modification during the process. It is insoluble in cold but easily soluble in hot water, and also in alcohol and ether. Its salts are mostly soluble in water. Nascent hydrogen has no effect on the acid either in acid or alkaline solution; with HI it is reduced to a valeric acid. Bromine forms a *dibrom-valeric acid*, melting at 76° and giving an oily brom-butylene on boiling with caustic potash:

$$C_4H_7Br_2.CO.OK + 2KOH = C_4H_7Br + K_2CO_3 + KBr + OH_2.$$

The exact constitution of angelic acid is not yet known, and indeed its isomerism with α-β-dimethyl acrylic acid cannot be represented by the notation at present in use.

4. *Allyl acetic acid*, $C_3H_5.CH_2.CO.OH$, is a colourless oil of boiling point 182°, obtained by the decomposition of ethylic allyl-aceto-acetate.

Acids of the Formula $C_6H_{10}O_2$.

798. 1. *Ethyl crotonic acid, α-methyl β-eth-acrylic acid:*

$$CH_3.CH : C(C_2H_5).CO.OH,$$

is obtained as ethylic salt on treating ethylic dieth-oxalate (§ 750, 2) with PCl_3 and then with water. It forms square prisms melting at 41·5°, sublimes at ordinary temperatures, and gives butyrate and acetate on fusion with potash.

2. *Hydro-sorbic acid, α-propyl acrylic acid*, $C_5H_9.CO.OH$, is obtained from sobric acid by the action of sodium amalgam. It is only slightly soluble in water, is liquid at −18°, boils at 204°, and at 19° has a sp. gr. of ·969; fusion with potassic hydrate splits it up into acetic and butyric acids.

3. *Pyroterebic acid, a-isopropyl acrylic acid:*

$$(CH_3)_2.CH_2.CH:CH.CO.OH,$$

is obtained by the dry distillation of terebic acid, $C_7H_{10}O_4$. It is an oil boiling at 210°; fusing potash gives isobutyric and acetic salts.

Higher Members of the $C_nH_{2n-2}O_2$ *Series.*

799. These bodies are very imperfectly known, there being still many gaps in the series.

Cimicic acid, $C_{15}H_{28}O_2$, occurs in a free state in a beetle (*Rhaphigaster punctipennis*), from which it may be extracted by ether. It melts at 44°.

Hypogæic acid, $C_{16}H_{30}O_2$, exists in earth-nut oil (*Arachis hypogae*) along with arachic acid (§ 598), and also in the sperm oil of *Physeter macrocephalus.* It forms colourless needles, melting at 33° and soluble in alcohol and ether. It oxidises in the air and combines with bromine to form *dibrom-palmitic acid*, $C_{16}H_{30}Br_2O_2$, melting point 29°, which, on treatment with potash, gives *monobrom-hypogæic acid*, $C_{16}H_{29}BrO_2$.

Nitrous acid converts hypogæic acid into an isomeric *gæidic acid*, of melting point 39°, which does not oxidise in air or decompose on distillation.

800. *Oleic acid*, $C_{18}H_{34}O_2$, is found as a glycerine salt in nearly all fats, $C_3H_5(O.C_{18}H_{33}O)_3$. Almond, olive, and whale oils are especially rich in this salt. The acid is obtained by saponification with plumbic oxide and finally purified by means of its barium salt.

It is a colourless, tasteless oil, solidifying at 0°, and afterwards melting at 14°. It distils in superheated steam at about 250°. When distilled alone it splits up into a mixture of sebacic, caproic, caprylic acids, and other bodies. It rapidly oxidises in the air, and gives salts with the alkalies which are true soaps. It combines with bromine to form $C_{18}H_{34}Br_2O_2$, from which brom-oleic and stearolic acids may be obtained by the action of potassic hydrate.

Oleic acid is converted by nitrous acid into the isomeric *elaïdic acid*, forming leafy crystals of 45° melting point. This acid also forms a dibromide from which nascent hydrogen reduces the original acid. Oleic acid, when fused with alkalies, gives acetic and palmitic acids.

Ricinoleic acid, or *hydroxy-oleic acid*, $C_{18}H_{34}O_3$, stands in near relationship to oleic acid. Its glycerine salt is found in linseed oil. It also gives an isomeric crystalline modification, melting at 50°, on treatment with nitrous acid. It does not oxidise on exposure to air, and gives on dry distillation œnanthol, and with potash yields normal secondary octyl alcohol along with methyl-hexyl ketone and sebacic acid:

$$C_{18}H_{33}KO_3 + KOH + OH_2 = \underset{\text{Potassic sebate.}}{C_{10}H_{16}K_2O_4} + \underset{\text{Octyl alcohol.}}{C_8H_{18}O} + H_2$$

$$C_{18}H_{33}O_3K + KOH + OH_2 = C_{10}H_{16}K_2O_4 + \underset{\text{Methyl-hexyl ketone.}}{C_8H_{16}O} + 2H_2$$

(comp. § 453).

801. *Dœglic acid,* $C_{19}H_{36}O_2$, from the oil from the dœgling or bottle-nosed whale, melts at 16°.

Erucic acid, $C_{22}H_{42}O_2$, also called *brassic acid,* is obtained from rape-seed oil, mustard oil, and also from grape seeds or kernels. It is purified by means of its lead salt in similar manner to that already described for other members of the series. It forms long shining needles melting at 34°. With bromine it gives a dibromide, $C_{22}H_{42}Br_2O_2$, forming warty crystals melting at 42°–43°, decomposed by alcoholic potassic hydrate into *brom-erucic acid,* $C_{22}H_{41}BrO_2$, fusing at 33°–34°.

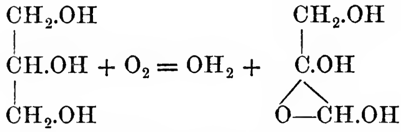
Dihydroxy-acids, $C_nH_{2n-3}(OH)_2O.OH$.

802. The only known member of this series is *glyceric acid, dihydroxy-propionic acid,* $C_3H_6O_4$, the product of the gentle oxidation of glycerine by nitric acid or by bromine and water.

For its preparation a mixture of equal parts of glycerine and water contained in tall glass cylinders is very slowly mixed with double its volume of nitric acid, of sp. gr. 1·3, by means of a long funnel tube reaching to the bottom of the liquid. After standing a few days, until the liquid has become homogeneous, it is evaporated to a syrup, which is then diluted with water and neutralised with plumbic carbonate. After several recrystallisations and treatment with animal charcoal the pure salt is decomposed by hydric sulphide. The filtrate, on evaporation, yields the free acid as a syrup.

Its salts are mostly soluble and crystallisable. The *calcic salt,* $(C_3H_5O_4)_2Ca + 2OH_2$, crystallises in concentrically grouped prisms. The *ethylic salt,* $C_3H_5(C_2H_5)O_4$, is a viscid liquid, boiling at 230°–240°, sp. gr. 1·193 at 6°, soluble in water, and easily decomposing into free acid and alcohol.

Glyceric acid is a monobasic acid and also a diatomic alcohol, and possibly has the constitution $CH_2(OH).CH(OH).CO.OH$, but the process of oxidation and constitution may also be expressed by the following equation :



On heating to 140° the acid gives a gummy substance, which is probably an ethereal anhydride (§ 707). At a higher temperature it gives off more water, and passes for the most part into pyro-racemic or pyruvic acid with a little pyro-tartaric acid :

$$C_3H_6O_4 = OH_2 + \underset{\text{Pyruvic acid.}}{C_3H_4O_3}$$

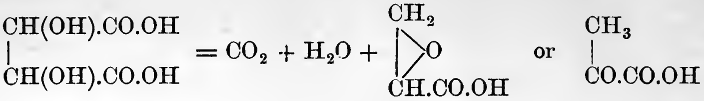
Treated with hydriodic acid it gives glycerine iodo-propionic acid (§ 744); with phosphoric chloride, the chloride of β-dichlor-propionic acid :

$$C_3H_6O_4 + PCl_3 = 3POCl_3 + 3HCl + C_3H_3Cl_2O.Cl.$$

Boiling potassic hydrate solution converts glyceric acid into oxalate and lactate. Melted potash gives acetate and formate.

803. The following bodies are related to this group :—

Aceto-formic acid, pyroracemic acid, or *pyruvic acid,* $CH_3.CO.CO.OH$, is obtained from glyceric acid, as above, or from tartaric acid:

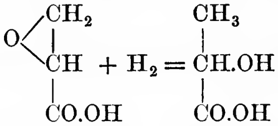


$$\begin{array}{l} CH(OH).CO.OH \\ | \\ CH(OH).CO.OH \end{array} = CO_2 + H_2O + \begin{array}{l} CH_2 \\ |\rangle O \\ CH.CO.OH \end{array} \quad \text{or} \quad \begin{array}{l} CH_3 \\ | \\ CO.CO.OH \end{array}$$

It is a liquid miscible with water and boiling between 165° and 170°, decomposing, however, slightly during distillation. Its monobasic salts are crystallisable, but lose this property on warming their solutions.

The acid cannot be obtained unchanged on acidifying its salts, but is converted into a syrupy non-volatile acid, giving pyro-tartaric acid on distillation.

Nascent hydrogen converts it into ordinary lactic acid, and by heating with hydric iodide either lactic or propionic acid may be produced, according to the temperature or relative quantities employed:



$$O\langle\begin{array}{l} CH_2 \\ | \\ CH \\ | \\ CO.OH \end{array} + H_2 = \begin{array}{l} CH_3 \\ | \\ CH.OH \\ | \\ CO.OH \end{array}$$

With bromine it forms an extremely unstable crystalline compound, $C_3H_4Br_2O_3$. At a temperature of 100° bromine gives a *dibrom-pyroracemic acid,* $C_3H_2Br_2O_3 + 2OH_2$, which forms large rhombic crystals. Phosphoric chloride converts it into dichlor propionic chloride. By long heating with baric hydrate solution salts of acetic, oxalic, and nitric acids are produced.

Propionyl formic acid, $CH_3.CH_2.CO.CO.OH$, is a colourless oily liquid, of sp. gr. 1·12 and boiling at 74°–78° under a pressure of 25 mm.

Butyryl formic acid, $CH_3.CH_2.CH_2.CO.CO.OH$, is a colourless liquid, boiling with slight decomposition at 180°–185° under ordinary atmospheric pressure.

Serine, sericine, $C_3H_7NO_3$, is related to glyceric acid in the same manner that glycocine is to glycollic acid or alanine to lactic acid. It is a product of the decomposition of silk by boiling dilute sulphuric acid.

Serine crystallises in hard prisms, soluble in cold water, but insoluble in alcohol. It has a faintly sweet taste, and behaves towards acids and bases like a glycine (§ 718); e.g. it combines one equivalent of an acid and allows one hydrogen atom to be replaced by a metal. Its salts are all crystallisable.

Nitrous acid converts it into glyceric acid :

$$C_3H_3(OH)(NH_2)O.OH + HO.NO = H_2O + N_2 \\ + C_3H_3(OH)_2O.OH.$$

Cystine, $C_3H_7NO_2S$, appears to be a sulphur derivative of serine. It has been found in urine and in the kidneys in very small quantity; in larger quantity in some forms of urinary calculi, from which it may be extracted by ammonia solution and obtained in minute colourless six-sided tabular crystals.

It is insoluble in water and alcohol, but dissolves in alkalies and acids, forming crystalline salts with the latter. It is non-volatile, and decomposes on heating with production of a most penetrating odour.

PROPARGYL COMPOUNDS.

804. By removal of two hydrogen atoms from allyl and substitution of a triple for a double carbon union, the primary radical *propargyl* is formed. The propargyl compounds therefore appear as allyene (§ 759), in which one hydrogen atom of the methyl group has been replaced by halogens or oxygen nuclei, &c.:

$$\begin{array}{c} CH \\ ||| \\ C \\ | \\ CH_3 \end{array}$$

allylene

$$\begin{array}{c} CH \\ ||| \\ C \\ | \\ CH_2 \end{array}$$

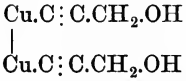
propargyl

805. *Propargylic alcohol*, $C_3H_4O = CH \vdots C.CH_2.OH$, is obtained from α-brom-allylic alcohol (§ 768) by heating with potassic hydrate and a little water in a vessel attached to an inverted condenser:

$$CH_2 : CBr.CH_2.OH + KOH = KBr + H_2O + CH \vdots C.CH_2.OH.$$

The excess of potassic hydrate is neutralised with carbonic anhydride, and the aqueous propargylic alcohol distilled off; potassic carbonate added to the distillate to saturation, the separated lighter layer removed, dried by fused potassic carbonate and rectified.

Propargylic alcohol is a colourless mobile liquid of burning taste and agreeable smell, miscible with water. Its sp. gr. is ·9628 at 21°, the vapour density 1·9; it boils at 115°. The vapour burns in air with a strongly luminous flame. It yields a siskin-green precipitate with ammoniacal cuprous chloride, which burns explosively on heating, and probably has the formula:



$$\begin{array}{l} Cu.C \vdots C.CH_2.OH \\ | \\ Cu.C \vdots C.CH_2.OH \end{array}$$

Ammoniacal argentic chloride gives a white precipitate of analogous composition, $Ag_2(C \vdots C.CH_2.OH)_2$. Both metallic compounds yield propargylic alcohol when treated with hydrochloric acid. It combines directly with bromine, and with strong hydrobromic acid regenerates α-brom-allylic alcohol.

It reacts on phosphorus tribromide, forming *propargylic bromide*, $CH \cdot C.CH_2Br$, a colourless liquid of sp. gr. 1·52 at 20° and boiling at 88°–90°, whilst acetylic chloride converts it into *propargylic acetate*, $CH \vdots C.CH_2.O.C_2H_3O$, a liquid of unpleasant odour, boiling at 125°.

Propargyl-ethyl ether, $C_5H_8O = CH \cdot C.CH_2.O.C_2H_5$, is obtained when alcoholic potassic hydrate acts on glyceryl trihaloids:

$$CH_2Cl.CHCl.CH_2Cl + 2KOH + KOC_2H_5 = 3KCl + 2H_2O$$
$$+ CH \vdots C.CH_2.O.C_2H_5 \text{ (comp. § 197),}$$

on allylene dibromide (§ 759):

$$CHBr{:}CBr.CH_3 + KOH + KOC_2H_5 = 2KBr + H_2O + CH{\vdots}C.CH_2.O.C_2H_5,$$

on dichlor glycid (§ 767):

$$CH_2{:}CCl.CH_2Cl + KOH + KOC_2H_5 = 2KCl + H_2O + CH{\vdots}C.CH_2.O.C_2H_5,$$

and on brom-propylene dibromide (§ 659). It is a colourless liquid of disagreeable, penetrant odour, of boiling point 81°–82° and sp. gr. ·83 at 7°. It gives a yellow precipitate with ammoniacal cuprous chloride, $Cu_2(C{\vdots}C.CH_2.O.C_2H_5)_2$, and a white in ammoniacal argentic nitrate of $Ag_2(C{\vdots}C.CH_2O.C_2H_5)_2$.

DERIVATIVES OF THE HEXAVALENT HYDROCARBON NUCLEUS, C_nH_{2n-4}.

MONOBASIC UNSATURATED ACIDS.

806. Although the first substitution products of the acids $C_nH_{2n-2}O_2$ (§ 792), and also ricinolic acid (§ 800), are monobasic acids of this group, it has been more convenient to consider them at another place.

COMPOUNDS OF THE DOUBLE ACID RADICALS, $C_{n'}H_{2n'}{:}(C{\equiv})_2$.

807. The chief representatives of this group are the dibasic acids and the derivatives of their oxy-radicals, the *diacidoxyls*, $C_{n'}H_{2n'}(CO)_2$. The only compounds known free from oxygen are some nitriles and a number of varied derivatives of the dicarbon nucleus $\vdots C.C \vdots$.

The dibasic acids stand to the monobasic acids in the same relation as the glycols to the monhydric alcohols. All metamorphoses of the monobasic acids can be suffered by them either singly or doubly. Thus they form two series of salts :

$$C_{n'}H_{2n'}\begin{matrix}.CO.OM\\.CO.OH\end{matrix}\qquad\qquad C_{n'}H_{2n'}\begin{matrix}.CO.OM\\.CO.OM\end{matrix}$$

Acid. Normal.

M representing either a metal or alkyl, &c., normal and acid amides :

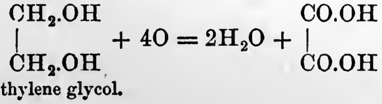
$$C_{n'}H_{2n'}\begin{matrix}.CO.NH_2\\.CO.NH_2\end{matrix}\qquad\qquad C_{n'}H_{2n'}\begin{matrix}.CO.NH_2\\.CO.OH\end{matrix}\text{ (amic acid)}$$

together with salts of the latter.

The formation of anhydrides and imides probably occurs in a different way to that in the fatty acids, the anhydro-oxygen atom or divalent imid group not being attached to two diacid oxyls, but to both bonds of a single diacid oxyl :

$$C_nH_{2n}\begin{matrix}.CO\\.CO\end{matrix}{>}O\text{, anhydride, and }C_nH_{2n}\begin{matrix}.CO\\.CO\end{matrix}{>}NH\text{, imide.}$$

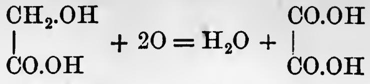
808. *Formation of Dibasic Acids.*—The dibasic acids can be prepared by oxidation of the double primary glycols, e.g.



$$\begin{matrix}CH_2.OH\\|\\CH_2.OH\end{matrix} + 4O = 2H_2O + \begin{matrix}CO.OH\\|\\CO.OH\end{matrix}$$

Ethylene glycol.

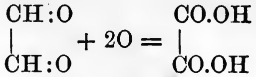
the primary alcohol acids, e.g.



$$\begin{array}{l} CH_2.OH \\ | \\ CO.OH \end{array} + 2O = H_2O + \begin{array}{l} CO.OH \\ | \\ CO.OH \end{array}$$

Glycollic acids.

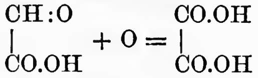
their aldehydes, e.g.



$$\begin{array}{l} CH:O \\ | \\ CH:O \end{array} + 2O = \begin{array}{l} CO.OH \\ | \\ CO.OH \end{array}$$

Glyoxal.

and the monobasic aldehyde acids, e.g.



$$\begin{array}{l} CH:O \\ | \\ CO.OH \end{array} + O = \begin{array}{l} CO.OH \\ | \\ CO.OH \end{array}$$

Glyoxylic acid.

Nearly all members of the series are formed by the oxidation of the fatty acids, $C_nH_{2n}O_2$, of high carbon contents, also from the acids of the oleic series, $C_nH_{2n-2}O_2$, and the acids, $C_nH_{2n-4}O_2$, and, in consequence, also from the monhydric alcohols and fats. Frequently in these cases several dibasic acids are formed at the same time, that first formed being further oxidised into carbonic anhydride, water, and an acid of less carbon contents :

$$C_nH_{2n}(CO.OH) + 3O = CO_2 + H_2O + C_{n-1}H_{2(n-1)}(CO.OH)_2.$$

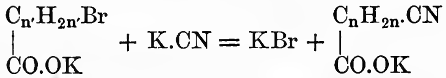
The following methods of preparation are accompanied with nucleus synthesis.

Alkylene dihaloids react on potassic cyanide, forming alkylene dicyanides, the nitriles of the radicals of the dibasic acids :

$$C_nH_{2n}Br_2 + 2K.CN = 2KBr + C_nH_{2n}(CN)_2,$$

which, by boiling with acids or alkalies, are converted into the dibasic acids and ammonia.

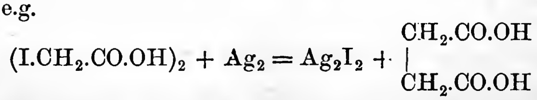
The monohalogen substitution derivatives of the fatty acids similarly yield the half-nitriles :



$$\begin{array}{l} C_{n'}H_{2n'}.Br \\ | \\ CO.OK \end{array} + K.CN = KBr + \begin{array}{l} C_nH_{2n}.CN \\ | \\ CO.OK \end{array}$$

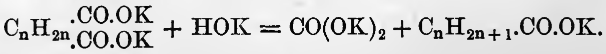
which also yield dibasic acids on boiling with acid or alkalies.

The moniodo fatty acids, on heating with finely divided silver, give up their iodine to the latter, the two residues uniting with one another, e.g.



$$(I.CH_2.CO.OH)_2 + Ag_2 = Ag_2I_2 + \begin{array}{l} CH_2.CO.OH \\ | \\ CH_2.CO.OH \end{array}$$

809. The dibasic acid can be converted into the fatty acid of next lower carbon contents—though always only in part—by fusing with potassic hydrate containing some water :



$$C_nH_{2n}\begin{array}{l} .CO.OK \\ .CO.OK \end{array} + HOK = CO(OK)_2 + C_nH_{2n+1}.CO.OK.$$

On electrolysis the alkaline salts of the dibasic acids yield alkylenes, containing two carbon atoms less, similarly to the formation of the dialkyls from the fatty acids :

$$C_{n'}H_{2n'}(CO.OK)_2 + H_2O = CO(OK)_2 + H_2 + CO_2 + C_{n'}H_{2n'}.$$

Compounds of the Dicarbon Nucleus, $\vdots C.C \vdots$.

Halogen Compounds.

810. *Dicarbon hexachloride*, C_2Cl_6, also termed *sesquichloride of carbon* and *perchlor ethane*, is the last chlor substitution product of ethane, and also therefore results from the action of chlorine, assisted by light and heat, on ethylic chloride, ethylene, and ethylidene dichlorides, the chlorides of the formula $C_2H_3Cl_3$ and $C_2H_2Cl_4$, and on ethinyl pentachloride, C_2HCl_5, also by the repeated action of alcoholic potassic hydrate and chlorine on ethylene dichloride (§ 473).

Perchlor-ethane forms colourless rhombic crystals of camphorous odour, which have sp. gr. 2 and boil at 182°. They are insoluble in water, but readily soluble in alcohol and ether.

On passing the vapour through red-hot tubes it decomposes into free chlorine and dicarbon tetrachloride :

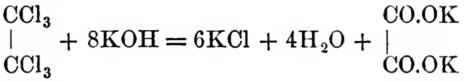
$$CCl_3.CCl_3 = Cl_2 + CCl_2:CCl_2.$$

Two chlorine atoms are removed by treatment with alcoholic potassic sulph-hydrate :

$$CCl_3.CCl_3 + 2KSH = 2KCl + S + SH_2 + CCl_2.CCl_2,$$

or with zinc and sulphuric acid.

At ordinary temperatures alcoholic potassic hydrate has no action ; on long heating it yields much oxalate :



$$\begin{matrix} CCl_3 \\ | \\ CCl_3 \end{matrix} + 8KOH = 6KCl + 4H_2O + \begin{matrix} CO.OK \\ | \\ CO.OK \end{matrix}$$

together with ethylene and oxidation products of the alcohol employed as a solvent.

Dicarbon tetrachloride, $C_2Cl_4 = CCl_2:CCl_2$, *perchlor ethylene*, is formed by the above decompositions of the hexachloride, and is readily obtained by heating the vapour of carbonic tetrachloride (§ 538). It is a colourless, mobile oil, of sp. gr. 1·649 at 0°, and boils at 117°. In sunlight it unites with two atoms of chlorine, forming the hexachloride, and also with bromine, yielding *dicarbon tetrachlor-dibromide*, $C_2Cl_4Br_2 = CCl_2Br.CCl_2Br$, small crystals of aromatic odour, of sp. gr. 2·3 at 21°, which decompose into their constituents at 200°.

On heating dicarbon tetrachloride in sealed tubes with nitric peroxide to 110°, they unite together and form *dinitro-tetrachlor ethane*, $C_2Cl_4(NO_2)_2$, a colourless crystalline mass, which decomposes into its constituents at 140°.

Bromine compounds of similar constitution and methods of preparation are known, as *dicarbon hexabromide*, $C_2Br_6 = CBr_3.CBr_3$, a colourless, crystalline body, difficultly soluble in alcohol and ether, readily in carbonic disulphide, and decomposing at 200° without fusion into bromine and

Dicarbon tetrabromide, $C_2Br_4 = CBr_2:CBr_2$, or *perbrom ethylene*, crystallises in beautiful plates, which melt at 50°. It is also formed by the decomposition of ethinyl pentabromide by alcoholic potassic hydrate.

Oxyhaloids.

811. *Perchlor-ethyl ether*, $C_4Cl_{10}O = (CCl_3.CCl_2)_2O$, is the last product of the action of chlorine, assisted by light and heat, on ethylic ether (comp. § 207). It crystallises in colourless scales of similar odour to chloral and perchlor ethane; it has sp. gr. 1·9 at 14·5° and melts at 69°. It decomposes at 300° into trichlor-acetylic chloride and perchlor ethane:

$$CCl_3.CCl_2.O.CCl_2.CCl_3 = CCl_3.CO.Cl + CCl_3.CCl_3.$$

Perchlor-ethyl ether loses four atoms of chlorine when boiled with alcoholic potassic sulphide, and is converted into *chloroxethose*, C_4Cl_6O:

$$(CCl_3.CCl_2)_2O + 2K_2S = 4KCl + S_2 + CCl_2:CCl.O.CCl:CCl_2,$$

a colourless liquid of agreeable *Spiraea*-like odour and sweet taste, of sp. gr. 1·654 at 21° and boiling at 210°. It is insoluble in water, but mixes in every proportion with alcohol and ether.

In sunlight it combines with chlorine, forming perchlor ether; with bromine it forms crystalline *chloroxethose tetrabromide*, $(CCl_2Br.CClBr)_2O$, which melts at 96° and is resolved into its components at 180°.

If the chlorine be added in presence of water, much chloracetic acid is formed:

$$(CCl_2:CCl)_2O + 3H_2O + 2Cl_2 = 4HCl + 2CCl_3.CO.OH.$$

812. *Perchlor ethylic formate*, $C_3Cl_6O_2 = CClO.O.C_2Cl_5$, the end product of the action of chlorine in sunlight on ethylic formate, is a colourless oil of strong, persistent odour, which boils at about 200°. When its vapour is passed through a tube heated to redness, it is decomposed into trichlor acetylic chloride and carbonic oxychloride:

$$CCl_3.CCl_2.O.CClO = CCl_3.CO.Cl + COCl_2.$$

Alcohol reacts with it, forming ethylic trichlor acetate and ethylic chlor-formate:

$$CCl_3.CCl_2.O.CClO + 2HO.C_2H_5 = 2HCl + CCl_3.CO.O.C_2H_5 + CClO.O.C_2H_5.$$

813. *Trichlor-acetylic chloride*, $C_2Cl_4O = CCl_3.COCl$, is an oil of persistent odour, which boils at 118° and has sp. gr. 1·603 at 18°. It deliquesces in air, being readily decomposed by water into trichlor acetic acid and hydrochloric acid:

$$CCl_3.COCl + H_2O = CCl_3.CO.OH + HCl.$$

It can be obtained from the latter by action of phosphoric chloride.

814. *Trichlor-acetic acid*, $C_2Cl_3HO_2 = CCl_3.CO.OH$, can be obtained from acetic acid by substitution, but is most readily prepared by allowing a mixture of chloral hydrate with three times its weight of nitric acid to stand for some days in sunlight. When the evolution of nitrous fumes has ceased, the mass is distilled from a retort, that portion coming over at 195° being pure trichlor-acetic acid. It solidifies in the cold to colourless rhomohedral crystals, which melt at 52·3°. Its salts are mostly crystalline and soluble.

Nascent hydrogen in aqueous solution (from potassium amalgam or electrolysis) converts it into acetic acid:

$$CCl_3.CO.OH + 6K + 2H_2O = CH_3.CO.OK + 3KCl + 2KOH.$$

On boiling with solution of potassic hydrate it decomposes into a carbonate and chloroform, the latter being readily further converted into a formate:

$$CCl_3.CO.OK + HOK = CHCl_3 + CO(OK)_2$$
$$CCl_3.CO.OK + 5HOK = CHO.OK + CO(OK)_2 + 3KCl + 2H_2O.$$

Boiling aqueous ammonia only produces the decomposition shown in the first equation.

Ethylic trichlor-acetate, $CCl_3.CO.O.C_2H_5$, obtained either by saturation of an alcoholic solution of the free acid with hydrochloric acid, or distillation with sulphuric acid, or by the action of trichlor acetylic chloride on alcohol, is a colourless oil boiling at 164°.

Ammonia converts it into alcohol and *trichlor-acetamide*, $CCl_3.CO.NH_2$, which crystallises in nacreous plates, melts at 136°, and boils at 239°. On heating with water to 100° it decomposes into ammonic carbonate and chloroform.

Perchlor methylic acetate, $C_3Cl_6O_2 = CCl_3.CO.O.CCl_3$, the last product of the action of chlorine on methylic acetate, is isomeric with, and closely resembles, perchlor ethylic formate. Its vapour is also decomposed into carbonic oxychloride and trichlor acetylic chloride on passing through a red-hot tube:

$$CCl_3.CO.O.CCl_3 = COCl_2 + Cl.CO.CCl_3.$$

Perchlor ethylic acetate, $C_4Cl_8O_2 = CCl_3\ CO.O.CCl_2.CCl_3$, is the product of the complete chlorination of ethylic acetate. It is a colourless liquid of chloral-like odour, boiling at 245° and having a sp. gr. of 1·79 at 25°. It is partly decomposed on distillation, completely on passing through a red-hot tube, yielding two molecules of trichlor acetylic chloride:

$$CCl_3.CO.O.CCl_2.CCl_3 = 2CCl_3.COCl.$$

815. *Tribrom-acetic acid*, $C_2Br_3O_2H = CBr_3.CO.OH$, is formed by oxidation of bromal (§ 778) with strong nitric acid. It is crystalline, melts at 135°, and boils at 250°. On boiling its potassic salt with potassic hydrate, it yields bromoform and potassic carbonate.

Tribrom-acetylic bromide, $CBr_3.COBr$, is obtained by heating dibrom-acetylic bromide (§ 779) with bromine to 200° in sealed tubes. It is a yellowish liquid, which boils somewhat above 220°, fumes in air, and yields tribrom-acetic acid with water.

Trisubstituted Aceto-nitriles.

816. *Fulminates.*—In presence of mercury or silver salts alcohol gives, on oxidation with nitric acid containing some nitrous acid, a crystalline explosive precipitate of the so-termed fulminates of silver and mercury. These have the same composition as the cyanates of those metals, but though having double the molecular weight, are not salts of a dicyanic acid, but from their products of decomposition would appear to be derivatives of aceto-nitrile (§ 547) in which one hydrogen atom has been replaced by nitryl (NO_2), the two others by metal.

Mercuric fulminate, *fulminating mercury*, $C_2N_2HgO_2$, is *mercury nitro-acetonitrile*, $CHg(NO_2).CN$. To prepare this compound 1 part of mercury is dissolved in 12 parts of nitric acid of sp. gr. 1·36, and 5½ parts of 90 % alcohol is then poured into the solution. As soon as the mixture is in violent reaction 6 parts more of alcohol are added slowly, to moderate the reaction. At first the mixture blackens, from separation of mercury, but this soon vanishes and is succeeded by crystalline flocks of mercuric fulminate, which fall to the bottom of the vessel. During the reaction large quantities of volatile oxidation products of alcohol, such as aldehyde, ethylic nitrate, &c., are evolved from the boiling liquid, whilst others, such as glycollic acid, remain in solution. The mercuric fulminate is then crystallised from hot water. It forms white, silky, delicate needles, which are difficultly soluble in cold water. In the dry state it is extremely explosive, detonating on heating or by friction or percussion, as also on contact with concentrated sulphuric acid. It is used, mixed with potassic nitrate, for filling percussion caps.

On adding copper or zinc to a hot saturated solution of the salt, metallic mercury separates, and readily soluble zincic or cupric fulminate is formed.

Argentic fulminate, fulminating silver, $C_2N_2O_2Ag_2$, diargento-nitro-acetonitrile, $C(NO_2)Ag_2.CN$, is prepared in similar manner to the mercury compound. It separates in fine white needles, which dissolve in 36 parts of boiling water and are very difficultly soluble in cold water. At above 100°, or on the weakest blow, fulminating silver explodes with fearful violence, even when covered with water.

On adding potassic chloride to a boiling solution of argentic fulminate as long as a precipitate of argentic chloride forms, there is obtained on evaporation brilliant white plates, of very explosive nature, of *potassic argentic fulminate*, $C(NO_2)KAg.CN$, from whose aqueous solution nitric acid precipitates a white powder of *hydric argentic fulminate*, $C(NO_2)HAg.CN$.

817. All attempts to prepare nitro-acetonitrile, $C(NO_2)H_2.CN$, from the fulminates have failed. On passing sulphuretted hydrogen through an aqueous solution of mercuric fulminate, mercuric sulphide is precipitated, but at the same time carbonic anhydride is evolved, and the solution contains ammonic sulpho-cyanate:

$$C(NO_2)Hg.CN + 2H_2S = HgS + CO_2 + (NH_4)S.CN.$$

Chlorine gas decomposes mercuric fulminate into mercuric chloride, chlorpicrin (§ 542), and cyanogen chloride:

$$C(NO_2)Hg.CN + 3Cl_2 = HgCl_2 + C(NO_2)Cl_3 + ClCN,$$

whilst bromine in the presence of water removes the metal, taking its place and yielding *dibrom nitro-acetonitrile*:

$$C(NO_2)Hg.CN + 2Br_2 = HgBr_2 + C(NO_2)Br_2.CN.$$

Dibrom nitro-acetonitrile crystallises from ether and alcohol in well-formed crystals insoluble in water. It melts at 50°, and commences to boil with decomposition at 130°.

Iodine acts like bromine and yields colourless monoclinic prisms of *diiodnitro-acetonitrile*, $C(NO_2)I_2.CN$, which melt at 86° with partial decomposition.

818. *Fulminuric Acid.*—By boiling mercuric fulminate with aqueous solutions of alkaline haloids, mercuric haloids and fulminurates are formed. Most usually ammonic chloride is employed to effect the decomposition; the solution is mixed with ammonia to precipitate the mercury as white precipitate, and ammonic fulminurate:

$$C_3N_3(NH_4)H_2O_3,$$

obtained by evaporating the filtrate. If potassic chloride be employed instead of ammonic chloride, potassic fulminurate is obtained in brilliant prisms. A solution of the ammonic salt gives with basic plumbic acetate a white precipitate of plumbic fulminurate. If this latter be suspended in water and decomposed with sulphuretted hydrogen, plumbic sulphide is precipitated and *fulminuric acid*, $C_3N_3H_3O_3$, remains in solution, and is left on evaporation in the form of a strongly acid syrup, which, on complete drying, solidifies to a crystalline mass. This latter decomposes with slight explosion when heated.

A mixture of strong sulphuric and nitric acids converts fulminuric acid into

819. *Trinitro-acetonitrile*, $C_2N_4O_6 = C(NO_2)_3.CN$, a colourless, camphor-like, crystalline mass, melting at 41·5°; it detonates violently at 220°, and is converted into carbonic anhydride and the ammonium compound of nitroform by water or alcohol at ordinary temperatures (§ 541).

Sulphuretted hydrogen converts trinitro-acetonitrile into *ammon-dinitro-acetonitrile:*

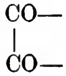
$$C(NO_2)_3.CN + 4H_2S = S_4 + 2H_2O + C(NO_2)_2(NH_4).CN,$$

crystallising in brilliant colourless needles, readily soluble in water, and which volatilise markedly with evolution of irritating fumes at 100°. Dilute sulphuric acid forms with it ammonic sulphate and *dinitro-acetonitrile*, $C(NO_2)_2H.CN$, forming large tables, and when treated with potassic hydrate it yields *potassium dinitro-acetonitrile*, $C(NO_2)_2K.CN$, with nitric acid again yields trinitro-acetonitrile.

The formation of trinitro-acetonitriles from fulminuric acid would characterise the latter as a dicarbon compound; neither its constitution nor molecular weight, however, can yet be settled.

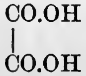
Trichlor-acetonitrile, $C_2Cl_3.N = CCl_3.CN$, is formed by heating trichlor acetamide with phosphoric anhydride, as an oil of penetrating odour, boiling at 83°–84° and of sp. gr. 1·439.

Compounds of the Oxalic Acid Radical,



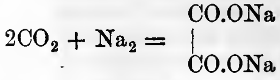
$$\begin{matrix} CO— \\ | \\ CO— \end{matrix}$$

820. *Oxalic acid*,



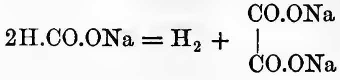
$$\begin{matrix} CO.OH \\ | \\ CO.OH \end{matrix}$$

. This acid is found widely distributed in nature in the form of salts—as potassic salt in the juices of different varieties of *Oxalis* and *Rumex*, as sodium salts in *Salsola Salicornia*. The calcium salt is often found in small crystals in plant cells, e.g. rhubarb, &c.; in the urine of men and animals it also often occurs, sometimes forming concretions in the bladder. It may be obtained artificially by the action of dry CO_2 on sodium at 350°–360°:



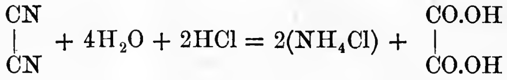
$$2CO_2 + Na_2 = \begin{array}{l} CO.ONa \\ | \\ CO.ONa \end{array}$$

by the decomposition of sodium formate by heat:



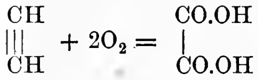
$$2H.CO.ONa = H_2 + \begin{array}{l} CO.ONa \\ | \\ CO.ONa \end{array}$$

and from its nitrile, dicyanogen, by the action of strong acids:



$$\begin{array}{l} CN \\ | \\ CN \end{array} + 4H_2O + 2HCl = 2(NH_4Cl) + \begin{array}{l} CO.OH \\ | \\ CO.OH \end{array}$$

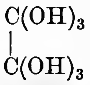
It is most readily obtained by the oxidation of many organic substances—alcohol, sugar, glycollic acid, acetylene, &c.:



$$\begin{array}{l} CH \\ ||| \\ CH \end{array} + 2O_2 = \begin{array}{l} CO.OH \\ | \\ CO.OH \end{array}$$

A common method of preparation is by the oxidation of sugar by nitric acid, 1 part sugar and 8 parts nitric acid, sp. gr. 1·38, being heated together; after evaporating the excess of nitric acid, the oxalic crystallises out and may be purified by recrystallisation from water. On the large scale it is obtained by melting some cheap form of cellulose—e.g. wood shavings, sawdust—with a mixture of caustic potash and soda. On treatment of the fused mass with a little cold water sodic oxalate remains for the most part undissolved.

The acid crystallises from its aqueous solution in colourless prisms of the probable formula:

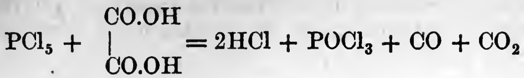


$$\begin{array}{l} C(OH)_3 \\ | \\ C(OH)_3 \end{array}$$

which dissolve in 9 parts cold water and 2½ parts of alcohol, and are very soluble in the boiling liquids. The crystals lose water in dry air, or at a temperature of 100°, and then have the composition $H_2C_2O_4$. It sublimes if carefully heated to 150° in fine white needles. By very quickly heating complete decomposition may be brought about, thus:

$$HO.CO.CO.OH = CO_2 + HCO.OH \text{ or } = CO_2 + CO + H_2O.$$

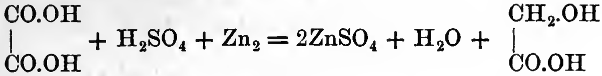
The latter products alone result when it is heated with sulphuric acid. With glycerine much formic acid (§ 567) is produced, some of the glycerine being reduced to allylic alcohol (§ 663). Oxidising agents convert it into carbonic anhydride and water. Phosphoric chloride acts as shown in the equation :



$$PCl_5 + \begin{array}{l}CO.OH\\ |\\ CO.OH\end{array} = 2HCl + POCl_3 + CO + CO_2$$

Fusing caustic alkalies produce carbonates.

Nascent hydrogen from zinc and sulphuric acid reduces oxalic acid to glycollic and glyoxylic acids :



$$\begin{array}{l}CO.OH\\ |\\ CO.OH\end{array} + H_2SO_4 + Zn_2 = 2ZnSO_4 + H_2O + \begin{array}{l}CH_2.OH\\ |\\ CO.OH\end{array}$$

821. *Oxalates.*—Oxalic acid is a strong dibasic acid, and gives with the alkali metals neutral and acid salts, and even salts with excess of acid (§ 575). Most of the other metallic salts are very insoluble, and are decomposed by strong mineral acids. The following selections must suffice as examples of the very numerous oxalates known :—

Dipotassic oxalate, $K_2C_2O_4,OH_2$; forms monclinic prisms easily soluble. *Hydric potassic oxalate,* KHC_2O_4,OH_2 ; forms rhombic prisms very difficultly soluble. *Potassic quadroxalate,* $KHC_2O_4, H_2C_2O_4,2H_2O$, commonly called salts of sorrel, crystallises in anorthic forms and dissolves in twenty parts water at 20°. Two *ammonic salts* are known isomorphic with the potassic salts. *Calcium oxalate,* $CaC_2O_4.OH_2$, or with $3OH_2$, is obtained as a white amorphous precipitate quite insoluble in water and acetic acid. In the cells of some plants and in urinary deposits it, however, sometimes forms crystals belonging to the rhombic system. Its last molecule of water may be expelled at 200°. The oxalates of mercury and silver are also white precipitates, which, when dried and heated, explode very violently, decomposing into metal and CO_2.

822. *Ethereal Salts of Oxalic Acid.*—*Neutral* and *acid salts* are known. The neutral are best obtained by long-continued heating of the particular alcohol with dried oxalic acid. They are decomposed even by cold water into the alcohol and acid, and also by alkalies. On heating with zinc and alkyl iodides they yield the alkyl salts of tertiary alcoholic acids (§ 705, 8) ; by the action of potassium, the salts of carbonic acid (§ 228).

Dimethylic oxalate, $(CH_3)_2C_2O_4$, prepared by distilling equal parts oxalic acid, methyl alcohol, and sulphuric acid, forms nacreous crystals of fusing point 51°, boiling at 162°.

Diethylic oxalate, $(C_2H_5)_2C_2O_4$, may be prepared in a similar manner to the above, and also by saturating a solution of oxalic acid in absolute alcohol with HCl gas and distilling. It is a mobile, colourless liquid of faint odour, boiling at 186°, and of sp. gr. 1·0824 at 15°.

Dipropyl oxalate, $(CH_3.CH_2.CH_2)_2C_2O_4$, boils at 209°–211°, sp. gr. 1·018.

Diisobutyl oxalate, $[(CH_3)_2 : CH.CH_2]_2C_2O_4$, boils at 224°–226°, sp. gr. = 1·002.

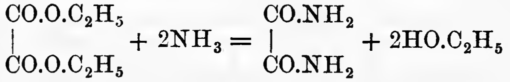
Salts of oxalic acid of the form $(C_nH_{2n+1})HC_2O_4$ are scarcely known in the free state. They decompose with great rapidity in contact with water. Their potassic salts may, however, be obtained as crystalline precipitates, e.g. potassic ethylic oxalate, $(C_2H_5)K.C_2O_4$.

823. Potassic ethylic oxalate, when acted upon by phosphor oxychloride, gives *ethyl-oxal chloride*; thus:

$$\begin{array}{l} CO.O.C_2H_5 \\ | \\ CO.OK \end{array} + POCl_3 = KPO_3 + KCl + 2 \begin{array}{l} CO.O.C_2H_5 \\ | \\ CO.Cl \end{array}$$

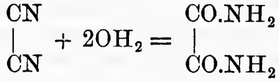
a liquid boiling at 140°, of sp. gr. 1·216, and fuming strongly in moist air. Water converts it into oxalic acid and ethylic chloride; with alcohol it forms the neutral salt

824. *Oxalyl Diamides.*—The neutral ethereal salts of oxalic acid are very easily converted by aqueous ammonia into the double amide of the acid, *oxamide*, $C_2H_4N_2O_2$:



$$\begin{array}{l} CO.O.C_2H_5 \\ | \\ CO.O.C_2H_5 \end{array} + 2NH_3 = \begin{array}{l} CO.NH_2 \\ | \\ CO.NH_2 \end{array} + 2HO.C_2H_5$$

The same body also results from the action of aldehyde on an aqueous solution of cyanogen:



$$\begin{array}{l} CN \\ | \\ CN \end{array} + 2OH_2 = \begin{array}{l} CO.NH_2 \\ | \\ CO.NH_2 \end{array}$$

also by the oxidation of hydrocyanic acid with hydric peroxide:

$$2HCN + H_2O_2 = C_2O_2(NH_2)_2.$$

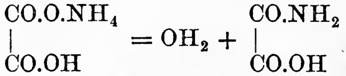
Oxamide is a white powder which requires about 10,000 times its weight of cold water for solution. It is taken up more freely by a hot saturated solution of calcic chloride, from which it crystallises in needles on cooling. It sublimes unchanged on careful heating. Heated with water to 200°, it is converted into neutral ammonic oxalate.

Alkyl oxalates are converted by alkylamines into dialkyl oxamides.

Dimethyl oxamide, $C_2O_2(N.CH_3.H)_2$, crystallises in needles soluble in hot water.

Diethyl oxamide, $C_2O_2(N.C_2H_5.H)_2$, is very similar.

825. *Acid Amides.*—By heating acid ammonic oxalate until carbonic anhydride begins to be evolved a mixture of oxamide and *oxamic acid* is left, from which the latter can be extracted by water:



$$\begin{array}{l} CO.O.NH_4 \\ | \\ CO.OH \end{array} = OH_2 + \begin{array}{l} CO.NH_2 \\ | \\ CO.OH \end{array} \quad \text{(oxamic acid)}$$

By evaporating its solution it may be obtained as a pulverulent substance of acid reaction, soluble in 58 parts of water at 18°. It melts at 173° and decomposes at the same time into water, formic acid, and oxamide. It recombines, when boiled with water, to acid ammonic oxalate. It acts towards metals as a monobasic acid and yields crystalline salts.

Ethereal oxamates may be prepared by acting on neutral ethereal salts of oxalic acid with alcoholic ammonia until oxamide begins to precipitate. Ethyl-oxal chloride also reacts with ammonia to form ethylic oxamate :

$$Cl.CO.CO.O.C_2H_5 + NH_3 = NH_4Cl + NH_2.CO.CO.O.C_2H_5.$$

Ethylic oxamate is best known. It crystallises in nacreous leaves, soluble in water and alcohol, and converted by ammonia into oxamide.

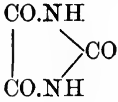
Isomeric with these ethereal salts are the *alkyl oxamic acids*, $C_2O_2\genfrac{}{}{0pt}{}{.N.(C_{n'}H_{2n'+1})H}{.OH}$, which result from heating the alkyl ammonic salts of oxalic acid to 180°.

Ethyl-oxamic acid, $C_2O_2\genfrac{}{}{0pt}{}{.N(C_2H_5)H}{.OH}$, forms six-sided tables and sublimes in fine needles. It melts at 120°.

Ethylic diethyl-oxamate, $C_2O_2\genfrac{}{}{0pt}{}{.N(C_2H_5)_2}{.O.C_2H_5}$, is obtained by reaction between ethylic oxalate and diethylamine (§ 262) as a liquid boiling at 254°. It gives a soluble salt with calcic hydrate, from which the free acid can be obtained by precipitation of the calcium with oxalic acid.

826. *Urea Derivatives.*—Uric acid stands in the same relation to carbonic acid that oxalic does to

Parabanic acid,

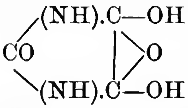


or *oxalyl urea.*

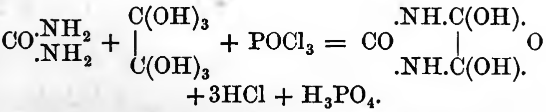
This body is obtained by oxidation of uric acid by warm nitric acid, or by heating uric acid with MnO_2 and sulphuric acid or with potassic chlorate and hydrochloric acid, by which latter oxidising mixture it may also be obtained from guanine.

Parabanic acid forms anhydrous, broad, colourless prisms, which dissolve in 21 parts of water at 8°.

It can also form a hydrate, which possibly has the constitution :



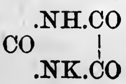
This hydrate may be prepared directly by the action of phosphoric oxychloride on a mixture of oxalic acid and urea, according to the equation :



$$CO\genfrac{}{}{0pt}{}{.NH_2}{.NH_2} + \genfrac{}{}{0pt}{}{C(OH)_3}{C(OH)_3} + POCl_3 = CO\genfrac{}{}{0pt}{}{.NH.C(OH).}{.NH.C(OH).}O$$
$$+ 3HCl + H_3PO_4.$$

It crystallises in compact rhombic prisms, which dissolve in 7½ parts of water at 8°.

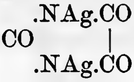
Oxalyl urea is not a true acid although it forms with alcoholic potash a crystalline metallic derivative :



$$CO\genfrac{}{}{0pt}{}{.NH.CO}{.NK.CO}$$

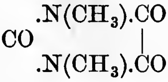
which is immediately decomposed by water into a salt of oxaluric acid.

A solution of parabanic acid gives with argentic nitrate solution, on careful addition of ammonia, a white precipitate, soluble in acids and excess of ammonia, of *diargento-oxalyl urea :*



$$CO\begin{matrix}.NAg.CO\\ \quad\ \ |\\ .NAg.CO\end{matrix}$$

which on heating with methylic iodide forms *dimethyl oxalyl urea,* or *cholestrophane* :

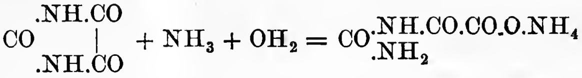


$$CO\begin{matrix}.N(CH_3).CO\\ \qquad\ \ |\\ .N(CH_3).CO\end{matrix}$$

crystallising in large shining rhombohedra. It dissolves in three parts cold water and cannot be sublimed. It was first discovered amongst the oxidation products of caffeïne.

On treating parabanic acid with aqueous alkalies salts of oxaluric acid, isomeric with parabanic hydrate, are produced.

827. *Oxaluric acid,* $C_3H_4N_2O_4$, is related to parabanic acid in the same manner that hydantoïc acid is to hydantoïn (§ 724). Oxaluric acid, or ammonic oxalurate, is most readily obtained by warming a solution of parabanic acid with ammonia :



$$CO\begin{matrix}.NH.CO\\ \quad\ |\\ .NH.CO\end{matrix} + NH_3 + OH_2 = CO\begin{matrix}.NH.CO.CO.O.NH_4\\ .NH_2\end{matrix}$$

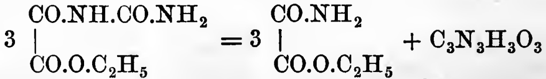
On acidifying with a mineral acid the oxaluric acid is separated as a white, difficultly soluble acid powder.

The ammonic salt is found in small amount in urine. Silver solutions yield a precipitate of *argentic oxalurate* : $C_3H_3AgN_2O_4$, silky needles soluble in hot water. $POCl_3$ warmed with oxaluric acid reproduces parabanic acid.

Ethylic oxalurate is formed by the reaction at ordinary temperatures between ethyl-oxal chloride (§ 823) and urea :

$$C_2H_5.O.CO.CO.Cl + NH_2.CO.NH_2 = HCl$$
$$+ C_2H_5.O.CO.CO.NH.CO.NH_2.$$

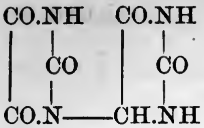
It crystallises in silky needles, only slightly soluble in alcohol, ether, or water in the cold. It melts between 160° and 170° and decomposes according to the equation :



$$3\begin{matrix}CO.NH.CO.NH_2\\ |\\ CO.O.C_2H_5\end{matrix} = 3\begin{matrix}CO.NH_2\\ |\\ CO.O.C_2H_5\end{matrix} + \underset{\text{Cyanuric acid.}}{C_3N_3H_3O_3}$$

On heating with alcoholic ammonia to 100° *oxaluramide,* $C_3H_5N_3O_3$, a white, almost insoluble powder, is produced.

828. *Oxalantine,* $C_6H_4N_4O_5,OH_2$. By the action of zinc and HCl on an aqueous parabanic acid solution this substance is produced, which probably has the constitution :



Allantoïn probably belongs to this group of bodies. It will, however, be described under the derivatives of uric acid.

Compounds of the Radical $CH_2:(C\equiv)_2$.

829. *Cyanacetic acid,* $CH_2\genfrac{}{}{0pt}{}{.CN}{.CO.OH}$. This acid is produced when 5 parts of ethylic monochlor acetate is boiled with 6 parts of potassic cyanide in 24 parts of water until the smell of hydrocyanic acid ceases to be perceived :

$$Cl.CH_2.CO.O.C_2H_5 + 2KCN + OH_2 = KCl + HO.C_2H_5 + HCN + CN.CH_2.CO.OK.$$

The solution is exactly neutralised with sulphuric acid evaporated to a small bulk, when an excess of strong acid is added, and the cyanacetic acid extracted by shaking out with ether. The acid is further purified by conversion into the plumbic salt, and decomposing this with hydric sulphide. Salts of this acid are all soluble, with the exception of those of mercury and silver. Cyanacetic acid is the half-nitrile of malonic acid, into which it is easily converted by boiling with alkali.

830. *Malonic acid,* $CH_2\genfrac{}{}{0pt}{}{.CO.OH}{.CO.OH}$. This acid is also best obtained pure by means of the lead salt from the crude product obtained by boiling cyanacetic acid with alkalies. It may also be obtained by careful oxidation of malic acid by potassic dichromate solution, and from ethylene lactic acid.

It crystallises in large plates, easily soluble in water and alcohol, of melting point 132°. It decomposes on heating into acetic and carbonic acids :

$$CH_2:(CO.OH)_2 = CH_3.CO.OH + CO_2,$$

corresponding to the decomposition of oxalic acid into carbonic and formic acids.

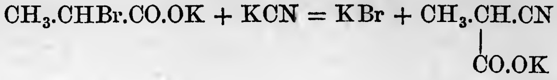
The alkali salts only of this acid are easily soluble in water. The baric salt, $CH_2:(CO.O)_2Ba,H_2O$, crystallises in groups of needles; the calcic salt, of similar appearance, is extremely difficultly soluble in water, the argentic and plumbic salts quite insoluble.

Barbituric acid, or *malonyl urea,* $CH_2:(CO.NH)_2:CO$, will be considered under the derivatives of uric acid.

Compounds of the Radical $C_2H_4:(C\equiv)_2$.

831. The hydrocarbon radical, $C_2H_4:(C\equiv)_2$, exists in two isomeric forms, accordingly as the group C_2H_4 occurs as ethylene or ethylidene. The dibasic acid, $C_2H_4\genfrac{}{}{0pt}{}{.CO.OH}{.CO.OH}$, is termed *succinic acid,* and is known in two forms, ordinary succinic and iso-succinic acid.

Iso-succinic or *ethylidene dicarboxylic acid,* $CH_3.CH:(CO.OH)_2$, is obtained, similarly to malonic acid, from the α-halogen compounds of propionic acid:



$$\mathrm{CH_3.CHBr.CO.OK + KCN = KBr +} \begin{array}{l} \mathrm{CH_3.CH.CN} \\ \qquad | \\ \qquad \mathrm{CO.OK} \end{array}$$

Potassic cyano-propionate.

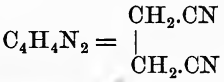
This latter body, which has not yet been isolated in a pure state, is boiled with potassic hydrate until ammonia ceases to be evolved, and the acid separated from the potassic salt after the method indicated for malonic acid.

Iso-succinic acid forms colourless crystals, subliming at 100°, melting at 130°, and decomposing at 150° into propionic and carbonic acids. This decomposition is determined by the fact that both CO.OH groups are combined in iso-succinic as in malonic acid to one carbon atom. It may therefore be termed *methyl malonic acid.*

The salts resemble those of malonic acid. It dissolves in 5 parts water at ordinary temperature.

Compounds of Ethylene Dicarbon, $\begin{array}{l} \mathrm{CH_2.C}\equiv \\ | \\ \mathrm{CH_2.C}\equiv \end{array}$

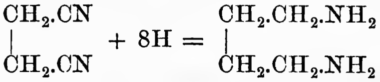
832. *Ethylene dicyanide*, or *ethylen dicarbo-nitrile:*



$$\mathrm{C_4H_4N_2} = \begin{array}{l} \mathrm{CH_2.CN} \\ | \\ \mathrm{CH_2.CN} \end{array}$$

is obtained by heating an alcoholic solution of ethylene dibromide with potassic cyanide. It is a crystalline mass melting at 37° and decomposing when heated.

Nascent hydrogen converts it into a butylene diamine:



$$\begin{array}{l} \mathrm{CH_2.CN} \\ | \\ \mathrm{CH_2.CN} \end{array} + 8\mathrm{H} = \begin{array}{l} \mathrm{CH_2.CH_2.NH_2} \\ | \\ \mathrm{CH_2.CH_2.NH_2} \end{array}$$

It gives ordinary succinic acid on saponification with alkalies.

833. *Succinic acid, ethylene dicarboxylic acid,* $\begin{array}{l} \mathrm{CH_2.CO.OH} \\ | \\ \mathrm{CH_2.CO.OH} \end{array}$, is found in amber, in wormwood and mountain ash berries (*Sorbus aucuparia*), and in many animal fluids. It is a regular product of the alcoholic fermentation of sugar and of the oxidation of fatty acids of high molecular weight. It is also formed by reduction of malic and tartaric acids, either by hydriodic acid or fermentation, and by the action of nascent hydrogen in maleic and fumaric acids.

Succinic acid is obtained on a large scale by the distillation of waste amber in iron retorts. The distillate is evaporated and boiled with nitric acid to destroy colouring matters, and crystallised from water.

It is also obtained by the fermentation of malic acid in alkaline solution by means of old cheese. The mixture of crude calcic malate, old cheese, and water is allowed to stand for some days at 30° or 40°, after which the precipitate is decomposed with sulphuric acid.

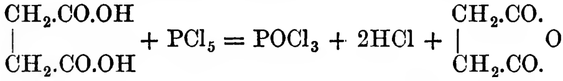
Succinic acid forms colourless monoclinic prisms, soluble in 17 parts of water at 18°, in 3 parts at 100°. It begins to sublime at 120°, and melts about 180°. It decomposes into anhydride and water at 235°.

By electrolysis carbonic acid, hydrogen, and ethylene are produced. In contact with uranium salts in sunlight it splits up into carbonic and propionic acids. The same reaction takes place when it is fused with alkalies.

Succinates of the alkalies are all easily soluble; salts with other metals are difficultly soluble or insoluble in water. Calcic succinate is somewhat soluble, and may be obtained in crystals, $C_2H_4{:}(CO.O)_2Ca_3OH_2$.

834. *Ethereal Salts of Succinic Acid.*—Many of these are known. Those of the monatomic alcohols are best obtained by warming a mixture of the acid and alcohol with sulphuric acid, washing with water, and rectification. *Ethylic succinate*, $C_2H_4\begin{matrix}.CO.O.C_2H_5\\.CO.O.C_2H_5\end{matrix}$, is a colourless, pretty mobile liquid, of sp. gr. 1·0718 at 0° and boiling point 217°. It does not dissolve in water, but is slowly decomposed by it.

835. *Succinic anhydride*, $\begin{matrix}CH_2.CO.\\|\\CH_2.CO.\end{matrix}O$, is prepared by repeated distillation of succinic acid alone, but better with phosphoric chloride:

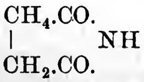


$$\begin{matrix}CH_2.CO.OH\\|\\CH_2.CO.OH\end{matrix} + PCl_5 = POCl_3 + 2HCl + \begin{matrix}CH_2.CO.\\|\\CH_2.CO.\end{matrix}O$$

It forms colourless crystals, melting at 120°, boiling at 250°. Boiling water slowly reconverts it into succinic acid.

836. *Succinyl dichloride*, $\begin{matrix}CH_2.CO.Cl\\|\\CH_2.CO.Cl\end{matrix}$. By heating one molecule of succinic acid with two of phosphoric chloride a liquid of suffocating odour is produced, of sp. gr. 1·39, which fumes strongly in moist air, boiling at 190°, and solidifies at 0° to tabular crystals. Water decomposes it into the succinic acid.

837. On agitating ethylic succinate with aqueous ammonia colourless needles of *succinamide*, $\begin{matrix}CH_2.CO.NH_2\\|\\CH_2.CO.NH_2\end{matrix}$, separate. They are difficultly soluble in water, alcohol, and ether. On carefully heating to 200° it is decomposed into ammonia and *succinimide:*



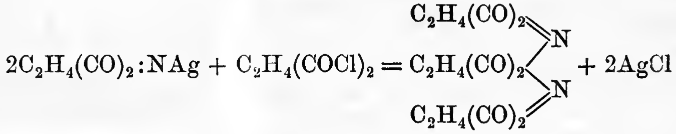
$$\begin{matrix}CH_4.CO.\\|\\CH_2.CO.\end{matrix}NH$$

The same body also results from heating succinic anhydride in dry ammonia gas and by the distillation of ammonic succinate. It dissolves in water and alcohol, and crystallises from the former with one molecule of water in rhombic tabular crystals, melting at 125°–126° and boiling at 287°–288°. It also sublimes in colourless needles.

On heating its solution with argentic nitrate and ammonia *argentic succinimide* is formed, $\begin{array}{l}CH_2.CO.\\ | \qquad NAg\\ CH_2.CO.\end{array}$, which, with excess of ammonia, gives *argentic succinamide*, $\begin{array}{l}CH_2.CO.NH_2\\ |\\ CH_2.CO.NAgH\end{array}$.

Succinimide gives with $Ba(OH)_2$ a *baric salt*, from which sulphuric acid liberates *succinamic acid*, $\begin{array}{l}CH_2.CO.NH_2\\ |\\ CH_2.CO.OH\end{array}$, which is very difficult to crystallise and easily reacts with water to form acid ammonic succinate.

If argentic succinimide be treated with an ethereal solution of succinyl chloride, argentic chloride separates, and the liquid on evaporation yields colourless prisms of *trisuccindiamine*:



$$2C_2H_4(CO)_2{:}NAg + C_2H_4(COCl)_2 = \begin{array}{l}C_2H_4(CO)_2\!>\!N\\ C_2H_4(CO)_2<\\ C_2H_4(CO)_2\!>\!N\end{array} + 2AgCl$$

Succinuric acid, corresponding to oxaluric acid (§ 827), is formed on heating equal molecules of succinic anhydride and urea to 120°:

$$\begin{array}{l}CH_2.CO.\\ | \qquad\qquad O\\ CH_2.CO.\end{array} + NH_2.CO.NH_2 = \begin{array}{l}CH_2.CO.OH\\ |\\ CH_2.CO.NH.CO.NH_2\end{array}$$

It forms colourless scaly crystals, melting with decomposition at 203°.

Compounds of the Radical $C_3H_6(C\equiv)_2$.

838. Only dibasic acids and some other diad derivatives belonging to this hydrocarbon residue are known; they are—

1. *Propane a-dicarboxylic* or *glutaric acid*:

$$\begin{array}{l}CH_2.(CO.OH)\\ |\\ CH_2.CH_2.CO.OH\end{array}$$

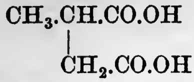
which may be obtained from dibromo-propane, $CH_2.Br.CH_2.CH_2.Br$, and by the decomposition with alcoholic potash of the product of the action of ethylic sod-aceto-acetate on ethylic α-iodo-propionate.

The acid forms broad four-sided prisms, melting at 98°. It distils if rapidly heated at about 290°; when slowly heated there is a partial production of anhydride.

2. *Ethyl-malonic acid*, $CH_3.CH_2.CH{:}(CO.OH)_2$, by treating ethylic α-brombutyrate (§ 747) with alcoholic potassic cyanide and subsequent saponification of the crude nitrile (see malonic acid). It forms small rhombic prisms, melting at 112°, and decomposes at 160° into CO_2 and butyric acid.

Its calcium salt, $C_5H_6CaO_4,H_2O$, is more soluble in cold than in hot water. The copper salt, $C_5H_6CuO_4,3H_2O$, forms fine blue tables. The plumbic salt is very insoluble.

3. *Pyrotartaric acid*, or *methyl succinic acid :*



$$\begin{array}{l}CH_3.CH.CO.OH\\ \quad\ \ |\\ \quad\ \ CH_2.CO.OH\end{array}$$

is prepared by heating tartaric acid with strong HCl to 180°, or by mixing it with sand or pumice and heating, whereby the formation of pyrosuccinic acid is avoided (§ 803). It is also obtained by the action of heat on aceto-formic and glyceric acids; by the action of nascent hydrogen on citraconic, itaconic, and mesaconic acids; by the saponification of dicyano-propane, $CH_3.CH(CN).CH_2(CN)$, from allyl iodide; from ethylic aceto-methyl succinate and alcoholic potash; and by fusing gamboge with potash.

It forms rhombic prisms melting at 112°; on rapidly heating and distilling it is resolved into water and methyl succinic anhydride, a liquid boiling at 245°. Its salts are mostly crystalline and insoluble.

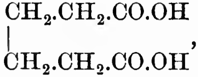
4. *Dimethyl-malonic acid*, $(CH_3)_2C:(CO.OH)_2$, prepared from dimethyl brom-acetic acid (brom-isobutyric). It forms four-sided prisms, much less soluble in water or alcohol than the isomeric acids, sublimes about 120°, and melts at 170°. It is very stable against oxidation.

Higher Homologues.

839. The acids, with the exception of rocellic, are also obtainable by the oxidation of the higher fatty acids by means of nitric acid, and several have also been synthesised by the aid of ethylic aceto-acetate derivatives.

Of acids of the formula $C_6H_{10}O_4$ there are known—

1. *Adipic, acid,*



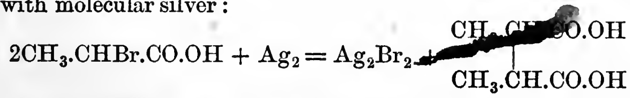
$$\begin{array}{l}CH_2.CH_2.CO.OH\\ |\\ CH_2.CH_2.CO.OH\end{array}$$

, is most readily obtained by heating glycerine *α*-iodo-propionic acid (§ 744) with finely divided silver to 150°:

$$2I.C_3H_4O.OH + Ag_2 = Ag_2I_2 + C_6H_8O_2(OH)_2.$$

An isomeric acid is simultaneously formed. Adipic acid may be crystallised from water in fine prisms, which melt at 148°. Its ammonic salt forms very beautiful rhombic plates.

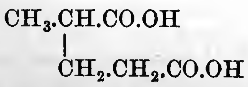
2. *Dimethyl succinic acid* is prepared by heating *α*-brom-propionic acid with molecular silver:



$$2CH_3.CHBr.CO.OH + Ag_2 = Ag_2Br_2 + \begin{array}{l}CH_3.CH.CO.OH\\ \qquad\ |\\ CH_3.CH.CO.OH\end{array}$$

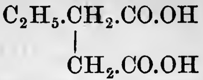
and by decomposing ethylic aceto-dimethyl succinate with potash. It is crystalline and melts at 166°.

3. *Methyl-propyl α-dicarboxylic acid :*

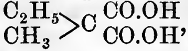


$$\begin{array}{l}CH_3.CH.CO.OH\\ \quad\ \ |\\ \quad\ \ CH_2.CH_2.CO.OH\end{array}$$

is obtained by decomposing the product of the action of ethylic *α*-iodo-propionate on ethylic sod-methyl aceto-acetate with potassic hydrate. It melts at 76°.

4. *Ethyl-succinic acid,*  $\begin{array}{c} C_2H_5.CH_2.CO.OH \\ | \\ CH_2.CO.OH \end{array}$, prepared by decomposing ethylic β-aceto-ethyl succinate with potash, melts at 98°.

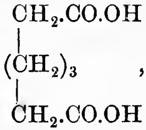
5. *Isopropyl malonic acid,*  $\begin{array}{c} CH_3 \\ CH_3 \end{array}\!\!>CH.CH.\!\begin{array}{c} CO.OH \\ CO.OH \end{array}$, prepared from ethylic isopropyl malonate, crystallises in prisms, melting at 83°.

6. *Ethyl-methyl malonic acid,*  $\begin{array}{c} C_2H_5 \\ CH_3 \end{array}\!\!>C\begin{array}{c} CO.OH \\ CO.OH \end{array}$, melts at 118°.

The two last acids split up on heating into the corresponding isopropyl acetic and ethyl-methyl acetic acids and carbonic acid.

Pentane Dicarboxylic Acids.

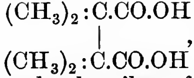
840. 1. *Pimelic acid,* $C_7H_{12}O_4$. An acid of this formula is obtained by fusing camphoric acid with potassic hydrate. It forms transparent triclinic crystals, melting at 114°. On dry distillation it gives a liquid anhydride, $C_7H_{10}O_3$, and water. Its calcic salt is very characteristic, being precipitated when calcic chloride is added to an ammoniacal solution of the acid and the mixture heated.

2. An isomeric acid, probably  $\begin{array}{l} CH_2.CO.OH \\ | \\ (CH_2)_3 \\ | \\ CH_2.CO.OH \end{array}$, prepared by oxidising suberone with nitric acid, and by heating furonic acid, $C_7H_8O_3$, with HI, melts at 103°.

3. *Diethyl malonic acid,* $(C_2H_5)_2C:(CO.OH)_2$, melts at 102°.

Hexane Dicarboxylic Acids, $C_8H_{14}O_4$.

841. 1. *Suberic acid* is obtained by long boiling of cork with concentrated nitric acid, or better from castor oil by saponification. It crystallises in long needles or plates, soluble in hot water, melts at 140°, and sublimes with partial decomposition between 150° and 160°. By heating with baric hydrate it gives normal hexane, C_6H_{14}.

2. *Tetramethyl succinic acid,*  $\begin{array}{c} (CH_3)_2:C.CO.OH \\ | \\ (CH_3)_2:C.CO.OH \end{array}$, obtained by heating ethylic brom-isobutyrate with molecular silver, forms small quadratic crystals, fusing at 95°.

Acids, $C_9H_{16}O_4$.

842. 1. *Azelaic acid,* lepargylic or anchoic acid, is obtained by oxidation of cork and many fatty substances; it is the chief product of the oxidation of castor oil, and is also formed on oxidation of stearolic acid. It forms lustrous plates or flat needles soluble in 400 parts cold water, easily soluble in hot water, alcohol, and ether; melts at 106°. Heated with baric hydrate, it gives normal heptane, C_7H_{16}.

2. Another acid, probably an isomer, is produced when butyrofuronic acid is heated with hydriodic acid. It melts at 118°.

843. *Sebacic acid, sebic acid,* $C_{10}H_{18}O_4$, formed by the dry distillation of oleic acid (§ 800) and by heating castor oil with sodic hydrate; crystallises from water in colourless shining plates, dissolving in 1,500 parts water at 10°, melting at 127°.

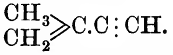
It yields octane by distillation with baric hydrate.

844. *Brassylic acid,* $C_{11}H_{20}O_4$, prepared by oxidation of behenolic acid, forms scaly crystals, difficulty soluble in hot water and melting at 109°.

Rocellic acid, $C_{17}H_{32}O_4$, obtained from *Lecanora tartarea* and *Rocella tinctoria,* forms colourless prisms, melting at 132°.

HYDROCARBONS, C_nH_{2n-4}.

845. *Valylene,* C_5H_6, prepared from isovalerylen dibromide (§ 769) by boiling with alcoholic potash, is a liquid of alliaceous odour, boiling at 50°. Like some other unsaturated hydrocarbons containing a C☰ group, it gives yellow precipitates with ammoniacal copper and silver solutions (§§ 752 and 759). From its method of production the constitution is probably



$$\genfrac{}{}{0pt}{}{CH_3}{CH_2}\!\!>C.C\vdots CH.$$

When carefully treated with bromine in a cooling mixture, a crystalline *valylene hexabromide,* $C_5H_6Br_6$, along with a liquid bromide, $C_5H_6Br_4$, is obtained.

Carpene, C_9H_{14}, is obtained by distilling calcic podocarpate. It is a mobile liquid, boiling at 155° and giving bromine derivatives, $C_9H_{13}Br$ and $C_9H_{12}Br_2$. It resinifies on exposure to air and resembles the terpenes in several respects.

DERIVATIVES OF THE HEXAVALENT ALCOHOL RADICALS, C_nH_{2n-4}.

846. In the hexhydric alcohols, $C_nH_{2n-4}(OH)_6$, the six hydroxyl groups are united to six different carbon atoms, so that there must be at least a hexacarbon nucleus. So far only derivatives of isomeric radicals, C_6H_8, are known.

Mannite, $C_6H_8(OH)_6$.

847. Mannite is very widely disseminated in the vegetable kingdom. It occurs in the leaves of *Syringia vulgaris* and *Ligustrum vulgare,* in numerous bulbs, as in those of *Cyclamen europaeum* and celery, in fungi and sea-weeds, in the sap of the larch, the bark of *Canella alba,* the exuded sap of apple and cherry trees, limes, &c. It occurs in large quantity in the sap of *Fraxinus Ornus,* which in the dry state forms commercial manna. It is prepared artificially from grape sugar by the action of the hydrogen evolved by sodium amalgam, or by reducing fermentations, as in the so-called mucous and butyric fermentations of sugar.

It is most readily obtained from manna. This is dissolved in half its weight of boiling water, some albumin added in order to clarify it, and filtered through a thick cloth. The mass which solidifies on cooling is pressed and obtained colourless by repeated fine division in water and pressing. Mannite can also be obtained pure by extracting manna with hot alcohol and crystallisation of the solution.

Mannite crystallises from alcohol in fine silky needles, from water in large, transparent, rhombic prisms. It dissolves in 65 parts of water at 16°, very readily at 100°. It is difficultly soluble in cold, readily in boiling alcohol, insoluble in ether. Its taste is intensely sweet; its melting point is above 160°. With metallic oxides it yields compounds in which a part of the hydroxylic hydrogen atoms have been replaced by metals (comp. glycerin, § 676).

On keeping a solution of mannite mixed with chalk and putrid cheese at a temperature not exceeding 40°, a fermentation occurs, in which lactic, butyric, and acetic acids and some alcohol are formed. By gentle oxidation, as by the standing of an aqueous solution with platinum black, it is first converted into a fermentable sugar, *mannitose*, $C_6H_8(OH)_6 + O = H_2O + C_6H_7(OH)_5O$, closely resembling fruit sugar, and from which, by further addition of oxygen, *mannitic acid*, $C_6H_{12}O_7$, is obtained. This latter yields saccharic acid on boiling with nitric acid, as also does mannite.

On heating mannite with concentrated hydriodic acid, *secondary normal hexylic iodide* is formed (§ 195). It follows from this that mannite must be considered as a derivative of normal hexane, and has the structural formula:

$$CH_2(OH).CH(OH).CH(OH).CH(OH).CH(CH).CH_2(OH).$$

848. *Haloid Derivatives of Mannite.*—By heating mannite to 100° with a large excess of concentrated hydrochloric or hydrobromic acid, two hydroxyl groups are replaced by halogen atoms. There are thus formed dihaloid tetrahydrates of the mannite radical (mannyl), which can be obtained in crystals by evaporation of the solution under a bell jar, in which are placed vessels containing potassic hydrate and sulphuric acid.

Mannite dichlor-hydrin, $C_6H_8Cl_2(OH)_4$, forms long colourless plates melting with evolution of hydrochloric acid at 174°; they dissolve in water, but are nearly or quite insoluble in alcohol or ether.

Mannite dibrom-hydrin, $C_6H_8Br_2(OH)_4$, is very similar to the foregoing, but is insoluble in water and melts with decomposition at 178°.

849. *Mannite Salts.*—As a hexavalent alcohol mannite reacts with strong mineral acids and the anhydrides of organic acids, yielding salts of mannite, of which only few have been prepared in a state of purity.

Mannite nitrate, $C_6H_8N_6O_{18} = C_6H_8(O.NO_2)_6$, *nitro-mannite*, or *mannyl hexanitrate*, is obtained by dissolving mannite in cold concentrated nitric acid, and separates in crystals on addition of concentrated sulphuric acid:

$$C_6H_8(OH)_6 + 6HO.NO_2 + 6H_2SO_4 = C_6H_8(O.NO_2)_6 + 6H_4SO_5.$$

This body is insoluble in cold water, but is readily dissolved by boiling alcohol and by ether, and separates from these solvents in fine silky needles, which melt at 108°. It burns with detonation at 120° and explodes violently under a short powerful blow:

$$C_6H_8(ONO_2)_6 = 6CO_2 + 4H_2O + 3N_2 + O_2.$$

Mannite sulphuric acid, $C_6H_8(OH)_3(O.SO_2.OH)_3$(?), is a hydric basic mannyl sulphate. It is prepared by dissolving mannite in strong sulphuric acid, and is separated in similar manner to ethysulphuric acid (§ 216), glycol, and glycerin sulphuric acids (§§ 518 and 690). As a strong acid it can exchange three atoms of hydrogen for metal, and yields readily soluble, difficultly crystallisable salts :

$$C_6H_8(OH)_3(O.SO_2.OM)_3.$$

The free acid is decomposed by water into dilute sulphuric acid and mannite.

Salts of organic acids cannot be prepared, as in the case of glycerin, by heating mannite with organic acids, as at the same time water is eliminated with formation of mannitan salts. Normal organic salts of mannite are obtained by long heating of mannite with the anhydrides of organic acids; there is thus obtained, e.g. :

$$C_6H_8(OH)_6 + 6(C_2H_3O)_2O = 6HO.C_2H_3O + C_6H_8(O.C_2H_3O)_6,$$

Mannyl Acetate.—This crystallises in white granules, which are little soluble in cold water, more readily in boiling water and alcohol, and melt at about 100°.

850. *Mannitan*, $C_6H_{12}O_5 = C_6H_8(OH)_4O$, or mannyl-oxide tetrahydrate, is prepared from mannite with direct elimination of a molecule of water by heating to 200°, and is also formed by long boiling with concentrated hydrochloric acid. Mannitan is a scarcely liquid syrup of strongly sweet taste, which is miscible with water and alcohol, insoluble in ether. By long contact with water, as by standing in moist air, or more quickly by boiling with baryta water, it takes up a molecule of water and is reconverted into mannite.

Halogen derivatives of mannitan are formed from the mannyl dihaloid tetrahydrates by boiling with water ; e.g.

$$C_6H_8Cl_2(OH)_4 = HCl + C_6H_8O(OH)_3Cl.$$

In addition to *mannitan chlorhydrin*, the corresponding *mannitan dibromhydrin*, $C_6H_8.O(OH_3)Br$, is also known. Both are crystalline bodies soluble in water, which melt below 100° and are converted into mannitan on long boiling with water :

$$C_6H_8O(OH)_3Cl + H_2O = HCl + C_6H_8(OH)_4O.$$

In the preparation of mannitan from mannite, by long boiling with hydrochloric acid, this chloride is without doubt formed as an intermediate product.

Salts of mannitan with organic acids are formed by the long heating of the latter with mannite at 200°–250°. The first products are diacid salts, from which, by similar treatment, the normal tetra-acid salts are obtained. The following are some of the salts prepared :—

Mannitan diacetate, $C_6H_8O(O.C_2H_3O)_2(OH)_2$, the *dibutyrate*, $C_6H_8O(O.C_4H_7O)_2(OH)_2$, and *tetrabutyrate*, $C_6H_8O(O.C_4H_7O)_4$, all three liquids soluble in ether. Palmitates and stearates have also been obtained as fatty masses.

851. *Dulcite*, or *melampyrite*, $C_6H_{14}O_6 = C_6H_8(OH)_6$, occurs in the sap of numerous plants, such as *Melampyrum nemorosum*, *Scrophularia nodosa*, *Evonymus europaeus*, &c. It occurs in largest quantity in the so-called dulcit manna from Madagascar, prepared from plants not yet determined, and is obtained therefrom by crystallisation from a hot aqueous solution.

Synthetically dulcite has been obtained by addition of hydrogen to lactose, by treatment of a solution of the latter with sodium amalgam.

Dulcite crystallises in large monoclinic prisms, melting at 188°–190°, which require 38 parts of water at 14° for solution. It is but little soluble in alcohol. By oxidation with nitric acid it yields mucic acid. The chemical behaviour of dulcite is very similar to that of mannite.

By heating with hydrochloric or hydrobromic acids it gives *dihaloid tetrahydrates*, crystallising in plates, which are but little soluble in water, and of which $C_6H_8Cl_2(OH)_4$ melts with decomposition at 180°.

With nitric and sulphuric acids dulcite yields *nitrodulcite*, $C_6H_8(O.NO_2)_6$. By heating to 180° with four times its weight of acetic anhydride it gives the *hexacetate*, $C_6H_8(O.C_2H_3O)_6$, crystallising in small brittle plates, melting at 171°. Heated to solution with $1\frac{1}{2}$ part of acetic anhydride and some glacial acetic acid, dulcite yields scales of a *diacetate*, $C_6H_8(OH)_2(O.C_2H_3O)_2$, melting at 176°; with acetic acid only it gives the *dulcitan salts:*

$$C_6H_8O(OH)_2(O.C_2H_3O)_2,$$

as an oily liquid, and $C_6H_8O(O.C_2H_3O)_4$ as a very bitter, resinous mass. By heating the latter with a molecule of acetic anhydride it is transformed into the hexacetate of dulcite.

Chlor-acetyl converts dulcite into the crystalline pentacetate chloride, $C_6H_8Cl(O.C_2H_3O)_5$, converted by water into

$$C_6H_8(OH)(O.C_2H_3O)_5,$$

crystallising in needles of melting point 165°.

852. A third isomeric of mannite, *sorbite*, $C_6H_{12}O_6$, occurs in the berries of the mountain ash (*Sorbus aucuparia*), and is found, as it is not fermentable, in the wine prepared from these by fermentation. It forms crystals containing $\frac{1}{2}$ molecule of water. In the dry state it melts at 110°–111°.

Isomerides of Mannitan.

853. Crystalline bodies isomeric with mannitan are found in several plants; their constitution must, however, be different, as no union with water and conversion into compounds of the mannite formula has been observed.

Pinite, $C_6H_{12}O_5$, occurs in the exudations of the Californian pine *Pinus lambertiana.* It forms hard, warty crystal masses of intensely sweet taste, which melt at 150° and whose solution rotates the plane of polarisation to the right.

Isodulcite, $C_6H_{12}O_5,H_2O$, is obtained, together with quercetin, by boiling quercitrin with dilute mineral acids. It forms large transparent crystals, which are readily soluble, and melt at 105°–110° with loss of their water of crystallisation.

DERIVATIVES OF THE HEPTAVALENT HYDROCARBON NUCLEUS, C_nH_{2n-5}.

MONOBASIC ACIDS OF THE SERIES $C_nH_{2n-4}O_2$.

854. Acids of this series, $C_nH_{2n-5}O.OH$ or $C_{n'}H_{2n'-3}.CO.OH$, are mostly prepared by the action of excess of alcoholic potassic hydrate on the halogen addition products of the members of the acryl oleic acid series :

$$C_{n'}H_{2n'-1}Br_2CO.OH + 3KOH = 2KBr + 3H_2O \\ + C_{n'}H_{2n'-3}.CO.OK,$$

or, what comes to essentially the same thing, on the first halogen substitution products of those acids :

$$C_{n'}H_{2n'-2}Br.CO.OH + 2KOH = KBr + 2H_2O + C_{n'}H_{2n'-3}.CO.OK.$$

In the carbon residue united to CO.OH either double union of neighbouring carbon atoms occurs twice, or else one triple union occurs, so that the acids can unite directly with four atoms of halogen.

By action of nitric acid the higher members of the series similarly unite with two atoms of oxygen, and yield monobasic acids of the formula $C_nH_{2n-4}O_4$, which further yield first half-aldehydes and later acids of the succinic series, whose carbon contents is equal to half that of the acid $C_nH_{2n-4}O_4$:

$$C_nH_{2n-4}O_4 + 3O = C_{\frac{n}{2}}H_{2\frac{n}{2}-2}O_4 + C_{\frac{n}{2}}H_{2\frac{n}{2}-2}O_3.$$

855. *Tetrolic acid,* $C_4H_4O_2$ or $C_3H_3CO.OH$. Either

$$CH_3.C \vdots C.CO.OH$$

or $CH_2 : C : CH.CO.OH$ is formed by heating chlor α-crotonic acid with alcoholic potassic hydrate on the water bath, and is obtained from the potassic salt first formed :

$$CH_3.CCl : CH.CO.OK + KOH = KCl + H_2O + C_3H_3.CO.OK,$$

by addition of sulphuric acid, and extracted from the aqueous solution by shaking with ether, and also by the action of carbonic anhydride on sodium allylene, $CH_3.C \vdots CNa$. It crystallises in rhombic tables, deliquescing in air, is also soluble in alcohol and ether, and melts at 76·5° and boils at 203°.

856. *Sorbic acid,* $C_6H_8O_2 = C_5H_7.CO.OH$, is obtained from the juice of unripe berries of the mountain ash by distillation, and passes over with the vapour of water as a yellow oil. This oil, on heating with solid potassic hydrate and acidulation, or by long boiling with strong hydrochloric acid, yields solid sorbic acid. It crystallises in long colourless needles, very difficultly soluble in cold, more readily in hot water and in alcohol, and melts at 134·5°. Although not distillable unchanged alone it passes over in the vapour of water. Its baric salt, $(C_5H_7.CO.O)_2Ba$, crystallises in silvery scales, which are readily soluble.

Ethylic sorbate, $C_5H_7CO.O.C_2H_5$, prepared by saturating the alcoholic solution of the acid with hydrochloric acid, is an oil of aromatic odour boiling at 195·5°.

Sorbic acid unites with nascent hydrogen, forming hydrosorbic acid (§ 798, 2), with bromine, according to the quantity of the latter, either to form the dibromide, $C_5H_7Br_2.CO.OH$, crystallising in small brilliant plates and melting at 94°–95°, or the tetrabromide, $C_5H_7Br_4.CO.OH$, or *tetrabrom-hexylic acid*, which is difficultly soluble in water, melts at 183°, and yields salts with the alkalies, barium, calcium, and zinc, which mostly crystallise in brilliant plates and decompose on boiling.

857. *Palmitolic acid*, $C_{16}H_{28}O_2 = C_{15}H_{27}CO.OH$, is obtained by heating hypogacic acid and gaidic acid dibromides (§ 799) with alcoholic potassic hydrate, and decomposition of the aqueous solutions of the potassic salt formed by mineral acids. It crystallises from alcohol and ether in fine silky needles, insoluble in water, melting at 42°, and combining directly with bromine to form the bromides $C_{16}H_{28}Br_2O_2$ and $C_{16}H_{28}Br_4O_2$.

Fuming nitric acid converts palmitolic acid into *palmitoxylic acid*, $C_{15}H_{27}O_2CO.OH$, crystallising in plates and melting at 67°, and further oxidises the latter with resolution into suberic aldehydic acid, $C_8H_{14}O_3$ (§ 782), and suberic acid, $C_8H_{14}O_4$ (§ 841).

Stearolic acid, $C_{18}H_{32}O_2 = C_{17}H_{31}.CO.OH$, is obtained from the dibromides of oleic and elaidic acids in long colourless prisms, melting at 48°, which are little soluble in cold alcohol. It volatilises without decomposition. Its salts are mostly crystalline, those of the alkalies having the properties of soaps. It does not unite with nascent hydrogen, but gives with bromine a liquid dibromide:

$$C_{18}H_{31}Br_2O.OH,$$

and a crystalline tetrabromide, $C_{18}H_{31}Br_4O.OH$, which melts at 70°. Nitric acid converts stearolic acid into *stearoxylic acid*:

$$C_{18}H_{32}O_4 = C_{17}H_{31}O_2.CO.OH.$$

This crystallises in brilliant plates, melting at 86°. Further action of the oxidising agent converts it, with decomposition of the molecule, into azela-aldehydic acid, $C_9H_{16}O_3$, and azelaic acid, $C_9H_{16}O_4$.

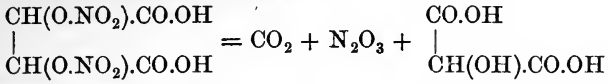
Behenolic acid, $C_{22}H_{40}O_2 = C_{21}H_{39}.CO.OH$, obtained by action of alcoholic potassic hydrate on erucic acid dibromide at 150° and on brassic acid dibromide at 210°–220°. It crystallises from alcohol in tufts of needles, melting at 57·5°, and gives crystalline bromides with two and four atoms of bromine. Concentrated nitric acid converts it into *behenoxylic acid*, $C_{21}H_{39}O_2.CO.OH$, brilliant plates melting at 90°–91°, brassylo-aldehydic acid, $C_{11}H_{20}O_3$, and brassylic acid, $C_{11}H_{20}O_2$.

Derivatives of the Radicals of Dibasic Hydroxy-Acids.

858. The compounds of this series are mostly dibasic acids, which are derived from the acids of the series $C_{n'}H_{2n'}(CO.OH)_2$ by substitution of halogen, hydroxyl, &c., for a hydrogen atom. The hydroxyl derivatives, $C_{n'}H_{2n'-1}(OH)(CO.OH)_2$, therefore, bear the same relation to these dibasic acids as that of the glycollic to the fatty acids.

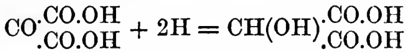
Tartronic Acid, $C_3H_4O_5 = CH(OH)(CO.OH)_2$.

859. Tartronic or *hydroxy-malonic acid* was first obtained by evaporating an aqueous solution of dinitro-tartaric acid:



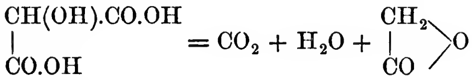
$$\begin{array}{l}CH(O.NO_2).CO.OH\\ |\\ CH(O.NO_2).CO.OH\end{array} = CO_2 + N_2O_3 + \begin{array}{l}CO.OH\\ |\\ CH(OH).CO.OH\end{array}$$

it is also formed by the action of nascent hydrogen on mesoxalic acid:



$$CO\begin{array}{l}.CO.OH\\ .CO.OH\end{array} + 2H = CH(OH)\begin{array}{l}.CO.OH\\ .CO.OH\end{array}$$

and by the oxidation of grape sugar by an alkaline copper solution. It crystallises in large colourless prisms, melting at 180°, with evolution of water and carbonic anhydride, and leaving an amorphous residue of glycollide (§ 713):



$$\begin{array}{l}CH(OH).CO.OH\\ |\\ CO.OH\end{array} = CO_2 + H_2O + \left.\begin{array}{l}CH_2\\ |\\ CO\end{array}\right> O$$

860. *Chloral cyanhydrin* is a derivative of the same carbon nucleus; it is obtained by the action of hydrocyanic acid on chloral hydrate:

$$CCl_3.CH(OH)_2 + HCN = H_2O + CCl_3.CH(OH).CN.$$

It crystallises in colourless prisms, melting between 60° and 61°, and is decomposed by alkalies into chloroform and metallic formate and cyanide.

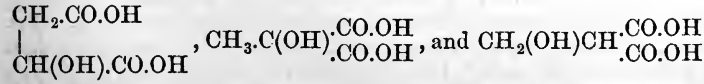
Trichlor-lactic acid, $CCl_3.CH(OH).CO.OH$, obtained by the action of aqueous acids on chloral cyanhydrin, is another derivative of the same carbon nucleus; it is crystalline and melts between 105° and 110°. Its salts readily decompose into formates and chloral:

$$CCl_3.CH(OH).CO.ONa = CCl_3.CHO + CHO.ONa.$$

Ethylic trichlor-lactate forms plates melting between 66° and 67°.

Malic Acid, $C_4H_6O_5 = C_2H_3(OH)(CO.OH)_2$.

861. Three isomeric acids are possible of this formula:



$$\begin{array}{l}CH_2.CO.OH\\ |\\ CH(OH).CO.OH\end{array},\ CH_3.C(OH)\begin{array}{l}.CO.OH\\ .CO.OH\end{array},\ \text{and}\ CH_2(OH)CH\begin{array}{l}.CO.OH\\ .CO.OH\end{array}$$

So far only two are known, which, however, appear not to be structural but physical isomers. One of them, natural malic acid, rotates the plane of polarisation to the right, whilst the artificial is optically inactive. Both of them are converted into ordinary succinic acid by heating with hydriodic acid, and must, therefore, correspond to the first of the three formulæ above given.

Natural or *optically active malic acid* occurs very widely disseminated in the vegetable juices, in the free state in sour apples, unripe grapes, and especially in quinces and unripe mountain ash berries.

It is best prepared from the boiled and filtered juice of the latter, which is then nearly saturated with milk of lime, so that it only possesses a feebly acid reaction. On continued boiling calcic malate, $C_2H_3(OH)\begin{smallmatrix}.CO.O\\ .CO.O\end{smallmatrix}\!\!>Ca,H_2O$, precipitates as a nearly insoluble crystalline powder. This is then added as long as it still dissolves to nitric acid diluted with ten times its weight of water. On cooling large brilliant, transparent crystals, difficultly soluble in water, of hydric calcic malate, $\left[C_2H_3(OH)\begin{smallmatrix}.CO.OH\\ .CO.O—\end{smallmatrix}\right]_2Ca,8H_2O$, separate; these are dissolved in hot water and precipitated with plumbic acetate. The washed, insoluble plumbic salt, $C_2H_3(OH)(CO.O)_2Pb$, is then suspended in water, decomposed by hydric sulphide, and the filtered liquid evaporated.

Malic acid crystallises only difficultly in cauliflower-like aggregates, which deliquesce in acid. It melts at below 100° and decomposes at 150°, or on long boiling with hydrochloric acid, into water and fumaric acid:

$$C_2H_3(OH)(CO.OH)_2 = H_2O + C_2H_2(CO.OH)_2.$$

Phosphoric chloride converts it into fumaric dichloride, $C_2H_2(CO.Cl)_2$.

Its aqueous solution rotates the plane of a polarised beam of light somewhat to the left (specif. rotation = − 5°). By heating with hydrobromic acid it is converted into brom-succinic acid:

$$C_2H_3(OH)(CO.OH)_2 + HBr = H_2O + C_2H_3Br(CO.OH)_2;$$

with strong hydriodic acid it yields ordinary succinic acid:

$$C_2H_3(OH)(CO.OH)_2 + 2HI = H_2O + I_2 + C_2H_4:(CO.OH)_2.$$

Chromic acid converts malic acid into malonic acid (§ 830); putrefaction ferments convert it into carbonic anhydride, acetic succinic (§ 833) and butyric acids. Fusing with potassic hydrate decomposes it into acetate and oxalate:

$$\begin{array}{l}CH(OH)CO.OK\\ \quad|\\ CH_2.CO.OK\end{array} + KOH = CH_3.CO.OK + KO.CO.CO.OK + H_2.$$

The alkaline malates are readily soluble, all others difficultly soluble; all are crystalline.

Diethylic malate, $C_2H_3(OH):(CO.O.C_2H_5)_2$, is obtained by saturating an alcoholic solution of malic acid with hydrochloric acid. The liquid, after standing for a long time, is neutralised with sodic hydrate and shaken with ether. On evaporation of the solution diethylic malate is obtained as a liquid soluble in alcohol, ether, and also in water, the latter soon decomposing it into alcohol and malic acid.

On mixing it with acetylic chloride a violent reaction occurs, in which there is formed :

$$C_2H_3(OH)(CO.O.C_2H_5) + Cl.C_2H_3O = HCl$$
$$+ C_2H_3(O.C_2H_3O)(CO.O.C_2H_5)_2,$$

Diethylic acetyl malate, a liquid boiling at 258°, insoluble in water, saponified by alkalies into ethylic alcohol and a malate and an acetate.

Alcoholic ammonia converts diethylic malate into *malamide,* $C_2H_3(OH):(CO.NH_2)_2$, which separates in anhydrous crystals on evaporation.

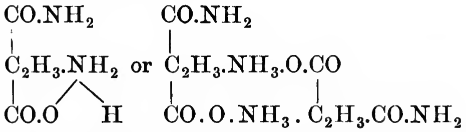
Asparagine and aspartic acid are most important derivatives of malic acid.

862. *Asparagine,* $C_4H_8N_2O_3$, occurs in the juices of many plants, especially in such parts as have been formed in the dark. It occurs largely in asparagus shoots, in the roots of *Althaea* and *Scorzonera,* also in the shoots evolved in the dark by leguminosæ.

To prepare it young shoots of vetch, grown in the dark, are strongly pressed, the filtered juice boiled to remove albuminoids, and the filtered liquid evaporated to a syrup. On long standing asparagine separates, and is purified by repeated crystallisation from hot water, being at first also heated with animal charcoal.

It forms hard, colourless, four-sided, rhombic prisms of the formula $C_4H_8N_2O_3,H_2O$. It is difficultly soluble in cold water, scarcely in alcohol ; it decomposes at higher temperatures without volatilisation. It rotates the plane of polarisation to the left.

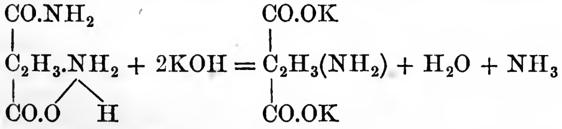
Asparagine is isomeric with malamide ; it behaves as though an amide of the alcohol group of malic acid, and also as an amic acid ; its structural formula is therefore :



$$\begin{array}{l} CO.NH_2 \\ | \\ C_2H_3.NH_2 \\ | \\ CO.O \quad H \end{array} \quad \text{or} \quad \begin{array}{l} CO.NH_2 \\ | \\ C_2H_3.NH_3.O.CO \\ | \qquad\qquad\quad | \\ CO.O.NH_3.C_2H_3.CO.NH_2 \end{array}$$

It yields with acids and bases compounds like those of glycocine (comp. § 718), and, like that body, unites with copper, &c. (§ 719). It is readily decomposed on boiling with acids or bases, yielding

863. *Aspartic acid,* $C_4H_7NO_4 = C_2H_3(NH_2):(CO.OH)_2$:

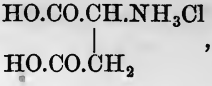


$$\begin{array}{l} CO.NH_2 \\ | \\ C_2H_3.NH_2 \\ | \\ CO.O \quad H \end{array} + 2KOH = \begin{array}{l} CO.OK \\ | \\ C_2H_3(NH_2) \\ | \\ CO.OK \end{array} + H_2O + NH_3$$

Aspartic acid occurs in sugar molasses, and in the product of decomposition of albuminoids, by boiling with sulphuric acid or by heating with bromine and water or zincic chloride. It crystallises in colourless rhombic prisms, which are scarcely soluble in alcohol and require 364 parts of water at 11° for solution. It rotates the plane of polarisation to the right.

Aspartic acid stands to malic acid in the same relation as glycocine to glycollic acid, and in consequence yields salts with both acids and alkalies.

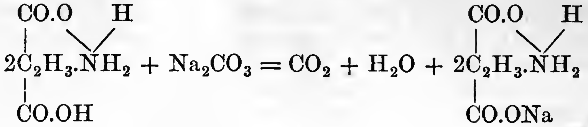
Aspartic acid hydrochloride,



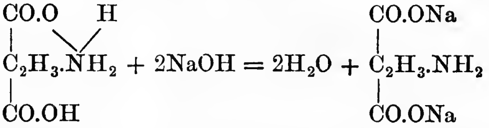
$$\begin{array}{l} HO.CO.CH.NH_3Cl \\ \quad\quad\;\; | \\ HO.CO.CH_2 \end{array}$$

, crystallises in rhombic prisms, whose solution is dextrorotary and has a strongly acid reaction.

Towards metallic carbonates aspartic acid behaves as a monobasic acid:



From strong basic hydrates it takes two equivalents of metal and yields salts of alkaline reaction:



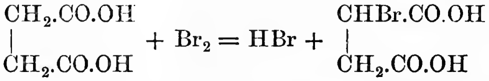
from which carbonic anhydride removes half the metal. All the metallic salts are dextrorotary.

Nitrous acid converts aspartic acid into optically active malic acid:

$$C_2H_3(NH_2):(CO.OH)_2 + HO.NO = H_2O + N_2 \\ + C_2H_3(OH):(CO.OH)_2.$$

864. *Optically inactive malic acid* can be prepared from succinic acid and from optically active malic acid.

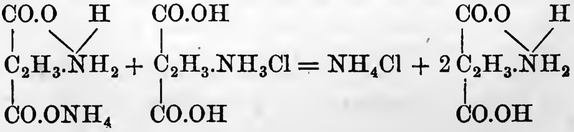
On heating succinic acid with a molecule of bromine and 15 times its weight of water to 150° in sealed glass tubes, *monobrom-succinic acid* is formed:



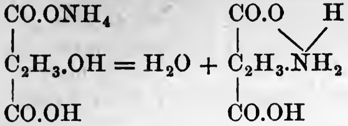
$$\begin{array}{l} CH_2.CO.OH \\ | \\ CH_2.CO.OH \end{array} + Br_2 = HBr + \begin{array}{l} CHBr.CO.OH \\ | \\ CH_2.CO.OH \end{array}$$

crystallising in needles, soluble in five times their weight of water, and converted on boiling with argentic oxide or alkalies into inactive malic acid or *hydroxy-succinic acid.*

The acid ammonic salt of optically active malic acid loses water when heated to 180°–200°, and is converted into a white powder, which on long boiling with hydrochloric acid goes slowly into solution as aspartic acid hydrochloride. This latter is then evaporated to dryness, to remove excess of hydrochloric acid, dissolved in water, one half of the solution neutralised with ammonia and the other half then added, when optically inactive aspartic acid is precipitated:

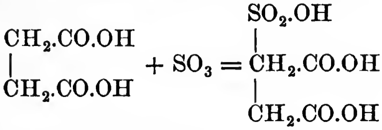


The previous conversion of ammonic malate is represented by the equation :



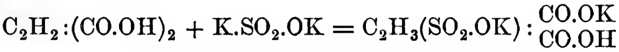
The optically inactive aspartic acid resembles the active completely, but is somewhat more soluble in water (in 208 parts at 15°). Similar inconsiderable differences are shown in the corresponding derivatives. Nitrous acid converts inactive aspartic into inactive malic acid, whose properties and reactions agree in all essentials with those of the natural acid.

865. *Sulphon-succinic acid,* $C_2H_3(SO_2OH)(CO.OH)_2$, is obtained by bringing together sulphuric anhydride and ethylene succinic acid :



$$\begin{array}{l}CH_2.CO.OH\\ |\\ CH_2.CO.OH\end{array} + SO_3 = \begin{array}{l}SO_2.OH\\ |\\ CH_2.CO.OH\\ |\\ CH_2.CO.OH\end{array}$$

and by long heating of fumaric or maleic acids with alkaline sulphites :



$$C_2H_2:(CO.OH)_2 + K.SO_2.OK = C_2H_3(SO_2.OK):\begin{array}{l}CO.OK\\ CO.OH\end{array}$$

It is a tribasic acid, is readily soluble, and crystallises indistinctly.

Acids of the Formula $C_5H_8O_5$.

866. 1. *Hydroxy-pyrotartaric Acids.*—Three isomeric acids of this formula have been prepared from the three isomeric pyrocitric acids (itaconic, citraconic, and mesaconic acids).

a. Itamalic Acid.—On heating with strong hydrochloric acid, itaconic acid unites with a molecule of HCl and yields *itamono-chlor-pyrotartaric acid :*

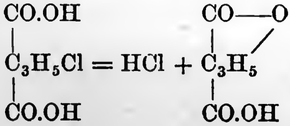
$$C_3H_4:(CO.OH)_2 + HCl = C_3H_5Cl:(CO.OH)_2,$$

which forms crystals melting between 140° and 145°. On boiling with water or alkalies it yields *itamalic acid :*

$$C_3H_5Cl:(CO.OH)_2 + H_2O = HCl + C_3H_5(OH):(CO.OH)_2.$$

The latter crystallises in long deliquescent needles, soluble in alcohol and ether, melts between 60° and 65°, and at higher temperatures loses a molecule of water and is reconverted into itaconic acid.

Paraconic acid may be regarded as the ethereal anhydride of itamalic acid. It is obtained together with that body by heating itachlor-pyrotartaric acid with water :



and can be obtained in the form of the calcic salt soluble in alcohol. It is crystalline, melts at 70°, and is readily soluble in water. It unites with hydrobromic acid, forming itabrom-pyrotartaric acid, and is converted into itamalic acid by strong bases.

b. Citramalic Acid.—Citraconic acid unites with hydrochloric acid, forming *citrachlor-pyrotartaric acid,* $C_3H_5Cl(CO.OH)_2$, which readily decomposes—mere warming of its aqueous solution sufficing—into hydrochloric and mesaconic acids, and from which citramalic acid cannot be prepared; but this can be obtained from the addition product of hypochlorous and citraconic acids, *chlor-citramalic acid:*

$$C_3H_4:(CO.OH)_2 + ClOH = C_3H_4Cl(OH):(CO.OH)_2,$$

when its aqueous solution is heated with zinc:

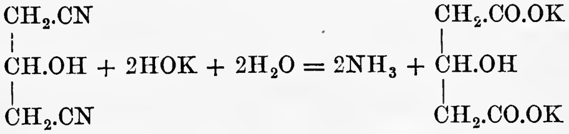
$$\begin{gathered}2C_3H_4Cl(OH):(CO.OH)_2 + Zn_3 = ZnCl_2 \\ + 2C_3H_5(OH):(CO.O)_2Zn + H_2.\end{gathered}$$

Citramalic acid is dibasic, amorphous, and deliquescent.

c. Mesamalic Acid.—Mesaconic acid gives with hydrochloric acid the crystalline mesachlor pyrotartaric acid, which melts at 129°–130°, and on boiling with water decomposes into mesamalic and hydrochloric acids. Mesamalic acid is deliquescent and melts at 60°.

All three acids are hydroxyl derivatives of pyrotartaric acid, into which they can be converted by heating with hydriodic acid.

2. *Glyceryl hydrate dicarbonic acid,* erroneously termed oxypyrotartaric acid, is prepared from dichlorhydrin. By heating this latter with alcohol and potassic cyanide, dicyanhydrin is formed, which on boiling with potassic hydrate yields ammonia and potassic glyceryl hydrate dicarbonate:



$$\begin{array}{l}CH_2.CN \\ | \\ CH.OH \\ | \\ CH_2.CN\end{array} + 2HOK + 2H_2O = 2NH_3 + \begin{array}{l}CH_2.CO.OK \\ | \\ CH.OH \\ | \\ CH_2.CO.OK\end{array}$$

The free acid forms colourless crystals, melting at 135° and soluble in water, alcohol, and ether.

3. *Hydroxy-glutaric Acid.*—Many protein bodies on decomposition yield, in addition to leucine, tyrosine, and aspartic acid, also a homologue of the latter, *glutamic acid:*

$$C_5H_9NO_4 = C_3H_5(NH_2):(CO.OH)_2,$$

which forms rhombic pyramids, difficultly soluble in water, and which on treatment with nitrous acid yields hydroxy-glutaric acid

This latter has only been obtained in the form of a scarcely crystallisable syrup, and forms amorphous salts. Hydriodic acid converts it into glutaric acid (§ 838, 3). The constitution of this compound is entirely unknown.

4. *Methyl hydroxy-succinic acid:*

$$CH_3.C(OH)(CO.OH).CH_2.CO.OH,$$

is prepared by heating ethylic aceto-acetate with half its weight of hydrocyanic acid at 100°, and then digesting with hydrochloric acid. It crystallises in deliquescent needles.

867. Probably *diaterebic acid*, $C_7H_{12}O_5$, and *terebic acid*, $C_7H_{10}O_4$, belong to this group. The first is only known in the form of salts, the latter in the free state also.

To prepare terebic acid, oil of turpentine is warmed to 80° with four parts of nitric acid of sp. gr. 1·25. As soon as the first violent action has ceased the resulting mass is heated on the water bath for twenty-four hours, with frequent addition of small quantities of nitric acid of sp. gr. 1·4. The liquid, evaporated to a third of its volume, is then mixed with much water, filtered if necessary, and evaporated to crystallisation. Hydric ammonic oxalate crystallises out with the terebic acid, from which the latter can be separated by recrystallisation from hot water.

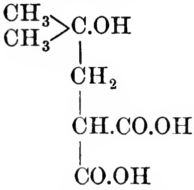
Terebic acid forms small, brilliant, colourless prisms, which dissolve in about 100 parts of cold water, more readily in alcohol and boiling water. It melts at 175°, sublimes below that temperature, decomposes on greater heating into carbonic anhydride and pyroterebic acid (§ 798, 3).

With carbonates it yields monobasic *terebates*, $C_7H_9MO_4$, which are mostly soluble in water. Strong bases, on the other hand, give the dibasic, mostly difficultly soluble and more crystallisable, salt of diaterebic acid:

$$C_7H_9KO_4 + KOH = C_7H_{10}K_2O_5,$$

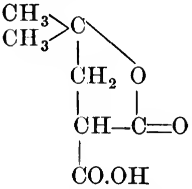
which on treatment with carbonic anhydride lose half their metal and are reconverted into terebates.

These reactions and the decomposition suffered by terebic acid on heating render the following constitutional formulæ probable:



$$\begin{array}{l} \left.\begin{array}{l}CH_3\\CH_3\end{array}\right>C.OH \\ \qquad | \\ \qquad CH_2 \\ \qquad | \\ \qquad CH.CO.OH \\ \qquad | \\ \qquad CO.OH \end{array}$$

Diaterebic acid.



Terebic acid.

Their relations to one another are the same as those of itamalic and paraconic acids.

THE GROUP OF 'CARBO-HYDRATES.'

868. The compounds belonging to this family contain either six or some whole multiple of six carbon atoms, and twice as many hydrogen as oxygen atoms. They are amongst the most important physiological compounds, generally forming the principal part of the organic matter of the vegetable organism, and also occur largely in the animal body.

The very numerous members correspond almost without exception to one of the formulæ $C_6H_{12}O_6$, $C_{12}H_{22}O_{11}$, and $C_6H_{10}O_5$, and stand to one another in very simple genetic relations.

The compounds corresponding to both the last expressions must be expressed as anhydrides of those of the first, and as a matter of fact are converted into them by action of ferments or by boiling with acids, water being combined :

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

and

$$(C_6H_{10}O_5)_n + nH_2O = nC_6H_{12}O_6.$$

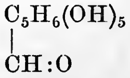
Although so far not a single one of these bodies has been prepared synthetically, nor the molecular weight yet been determined with certainty in a single case, yet something is known of the constitution of these bodies. They have, without exception, the properties of polyhydric alcohols, and some of them in addition behave like aldehydes. The compounds $C_6H_{12}O_6$ and $C_{12}H_{22}O_{11}$ are soluble in water, have a sweet taste, and are termed *sugars*, whilst a part of those having the atomic proportion $C_6H_{10}O_5$ cannot be dissolved unchanged by any liquid.

The Sugars, $C_6H_{12}O_6$. *Glucoses.*

869. The most widely disseminated and most important sugars of this group are the first aldehydes of the mannite bodies, $C_6H_{14}O_6$ (§ 846 and following), and can be converted into those hexhydric alcohols by the action of nascent hydrogen. As aldehydes they reduce the oxides of the noble metals, as also cupric oxide when free alkali is present. In addition they behave as pentahydric alcohols, i.e. can exchange five hydrogen atoms for acid radicals, forming true salts, also can exchange some of these hydrogen atoms for metal, which, however, is again removed by carbonic anhydride. Several of them are so decomposed by yeast, when in aqueous solution, that the main products are ethylic alcohol and carbonic anhydride. Their constitution can be expressed by the formula $C_5H_6(OH)_5.CH:O$. That the group $C_5H_5(OH)_5$, even if each hydroxyl group be united to a different carbon atom, can have varied constitutions, and therefore is the cause of true isomerism, requires no further proof. The number of possible isomers would be still further increased if, as with the single aldehydes of the formula $C_nH_{2n}O$, polymerisations also occurred, and physical isomerism may also occur.

There still remains the further possibility of the existence of hexhydric alcohols of the formula $C_6H_{12}O_6 = C_6H_6(OH)_6$, in whose carbon nuclei there must occur either one divalent union of neighbouring carbon atoms or the nucleus must be closed to a ring. Such bodies are, so far, not known with certainty, but it is quite possible that certain sugars which lack the properties of aldehydes, and also are incapable of fermentation, may belong to the category.

Grape Sugar, Glucose or Dextrose,



$$\begin{array}{l} C_5H_6(OH)_5 \\ | \\ CH:O \end{array}$$

870. Dextrose occurs in most sweet-tasting fruits, such as grapes, figs, cherries, plums, &c., often together with the isomeric fruit sugar. It can be obtained from these fruits by boiling and filtering the juice, evaporating to a syrup, when, on standing, it crystallises after a time in warty masses, and can be purified by crystallisation from hot alcohol. Dextrose occurs, together with lævulose, in honey, in small quantity in healthy blood and urine, and at times largely pathologically in the latter (especially in cases of *diabetes*). It also is found in small quantity in the liver when examined quickly after death; after the lapse of a little time it is found in large quantity, as the result of post-mortem changes in the glycogen contained in the liver. It is further obtained by the action of certain ferments or hot dilute acids on certain of the carbo-hydrates of the formulæ $C_{12}H_{22}O_{11}$ (e.g. from cane sugar together with lævulose) and $C_6H_{10}O_5$ (cellulose, starch, dextrin), by combination of water, and by similar action from numerous organic bodies which are ethereal or saline compounds of dextrose and are termed *glucosides* (e.g. salicine, phloridzine, amygdaline, &c.) On the large scale it is generally prepared by adding 10 parts of starch in portions to a boiling mixture of 1 part of sulphuric acid and 20 parts of water; after boiling for several hours the acid is neutralised with calcic carbonate, the solution freed from the separated calcic sulphate, decolourised by animal charcoal, and the syrup evaporated. This, on cooling, then solidifies to an indistinctly crystalline mass of grape sugar. Starch can also be converted into dextrose by the action of the diastase of malt. To obtain it pure it must be finally crystallised from alcohol.

From aqueous solution dextrose separates in colourless granular masses of the formula $C_6H_{12}O_6,H_2O$; from strong alcohol, anhydrous in fine needles, which unite to wart-like masses.

They first lose their water of crystallisation on slow heating below 80°; on quick heating to this temperature they melt, and an amorphous hygroscopic mass is obtained, which is slowly reconverted into crystals on exposure to moist air.

Dry dextrose dissolves in $1\frac{1}{3}$ part of cold water, 50 parts of 85 % alcohol at ordinary temperatures, but only about 5 parts at the boiling point.

All solutions of dextrose rotate the plane of polarisation strongly to the right; the specific rotatory power of freshly prepared solutions of both crystalline forms and of that dried without fusion $= 104°$. On keeping this diminishes slowly by boiling quickly until it becomes constant at $[a] = 56°$. This latter rotary power is also that of a freshly prepared solution of amorphous grape sugar rendered anhydrous by fusion, and of such as occurs in aqueous solution (therefore of that in urine).

By long heating to 170° dry dextrose loses a molecule of water and is transformed into *glucosane*, $C_6H_{10}O_5$, an amorphous mass of scarcely sweet taste, which stands to dextrose as mannitan does to mannite, and similarly can be reconverted into dextrose by slow addition of water, especially by boiling with dilute mineral acids.

The noble metals are precipitated in the metallic state from all their solutions by dextrose, mercury even being precipitated from mercuric cyanide. Cupric solutions are also reduced in the presence of free alkali. This latter reaction occurs slowly in the cold, very quickly on heating, and in the latter case gives pure anhydrous cuprous oxide. In the presence of free alkali basic bismuthous nitrate is also reduced.

The reduction of cupric salts is employed in a very useful volumetric method for the estimation of dextrose, one molecule of the latter in presence of much water causing the reduction of five molecules of cupric salt to cuprous oxide.

The copper is employed in the form of '*Fehling's solution.*' This is prepared by dissolving 34·64 grams of pure crystallised cupric sulphate in about 100 grams of water, mixed with a solution of 200 grams of potassic sodic tartrate in 600 cc. of sodic hydrate solution of 1·12 sp. gr., and the whole made up to 1,000 cc. by addition of water. 10 cc. of this solution will require for complete reduction ·05 gram of dextrose. After the reaction the salts of tartronic and several other organic acids are found in solution.

In presence of free alkalies dextrose can be oxidised by exposure to air; in absence of air an alkaline solution, on heating, turns brown, and after a time deposits humus-like bodies.

The decompositions of grape sugar in aqueous solution by yeast, chiefly into alcohol and carbonic anhydride, and by putrefaction ferments into lactic and later into butyric acids, with simultaneous formation of mannite, have been already mentioned at the respective places. Under other circumstances, at present not known with certainty, the so-called *mucous fermentation* occurs, whose chief products are a gummy body, lactic acid and mannite.

Mannite is also formed from dextrose by nascent hydrogen evolved with sodium amalgam. From this it is very probable, though not certain, that dextrose may be expressed by the formula:

$$CH_2(OH).CH(OH).CH(OH).CH(OH).CH(OH).CH:O.$$

The first oxidation products of dextrose are gluconic and saccharic acids.

871. *Dextrose Salts.*—Anhydrous dextrose dissolves slowly and without coloration in 1½ time its weight of concentrated sulphuric acid, and yields thereby a basic hydric sulphate corresponding in general to glycerine sulphuric acid. The formula of this *dextrose sulphuric acid* is not known, as, on account of its ready decomposability by water into dextrose and sulphuric acid, it can scarcely be prepared in a state of purity. Its baric salt is soluble.

Different acetates are obtained by heating dextrose with acetic anhydride. One part of dextrose with 2½ parts of acetic anhydride yields at the boiling point of the latter *dextrose diacetate*, $C_5H_6(OH)_3(O.C_2H_3O)_2.CHO$, as a colourless amorphous mass, melting below 100°, of very bitter taste, readily soluble in alcohol and water, which by heating to 160° with water is rapidly decomposed into acetic acid and dextrose. If it is heated for a long time to 140° with double its weight of acetic anhydride *dextrose triacetate*, $C_5H_6(OH)_2(O.C_2H_3O)_3.CHO$, is formed as a colourless solid mass, difficultly soluble in water, readily in alcohol and ether.

On heating dextrose with large excess of acetylic chloride a pretty energetic reaction occurs, and after evaporation there remains acetochlor-hydrose, i.e. *dextrose chloride tetracetate:*

$$C_5H_6Cl(O.C_2H_3O)_4.CHO,$$

as a colourless crystalline body, very readily decomposed by water and converted by well-cooled strong nitric acid into *dextrose nitrate* *tetracetate*, $C_5H_6(O.NO_2)(O.C_2H_3O)_4.CHO$, which crystallises in rhombic tables and prisms melting at 145°, is insoluble in water, but soluble in alcohol.

872. *Metallic Compounds of Dextrose.*—Like all polyhydric alcohols dextrose combines with metals when in contact with basic hydrates. The resulting compounds are mostly soluble in water, are decomposed by carbonic anhydride into dextrose and a carbonate, and are oxidised and turn brown on exposure to atmospheric oxygen.

On mixing alcoholic solutions of dextrose and potassic hydrate, a transparent jelly of *potassium dextrose* separates, which soon discolours and decomposes. The barium and calcium compounds are also soluble in water. An insoluble lead compound is obtained by precipitating a solution of dextrose by basic plumbic acetate, as an amorphous precipitate containing three atoms of lead to two molecules of sugar.

In presence of alkali cupric oxide is largely dissolved to a deep blue liquid, which soon deposits cuprous oxide.

A beautiful crystalline compound, *dextrose sodic chloride:*

$$2C_6H_{12}O_6,NaCl,H_2O,$$

is formed by mixing solutions of dextrose and common salt and evaporating slowly. This often separates spontaneously from diabetic urine.

Lævulose, or Fruit Sugar, $C_6H_{12}O_6$.

873. Lævulose frequently accompanies dextrose in the juices of sweet fruits, and together with the latter constitutes honey. It is formed together with dextrose in the decomposition of cane sugar by ferments or by boiling with acids, and is formed alone in the corresponding transformation of inulin. As lævulose does not crystallise, its purification is extremely difficult. The separation from dextrose is best effected by means of the difficultly soluble lime compound.

Dried at 100°, lævulose forms a gummy, deliquescent mass, which is pretty soluble in mediumly concentrated spirit, but is insoluble in absolute alcohol. The solutions rotate the plane of polarisation to the left, the specific rotary power $= -104°$.

Towards ferments, bases, oxides of the noble metals, and alkaline cupric solutions it behaves exactly like dextrose. Heated to 170°, it is converted into *lævulosane*, $C_6H_{10}O_5$, which can be reconverted into lævulose. On oxidation it yields saccharic acid.

Mannitose, obtained from mannite by moderated oxidation, bears a great resemblance to lævulose, but it is distinguished by its optical inactivity.

Lactose, $C_6H_{12}O_6$.

874. Lactose is formed from milk sugar by treatment with ferments or dilute acids, together with another sugar which appears to be dextrose. On evaporating the liquid lactose crystallises first in leafy and warty crystals. It has a greater dextrorotary power than dextrose, undergoes alcoholic fermentation when mixed with yeast, and reduces alkaline cupric salts to cuprous oxide. It is distinguished from dextrose by giving no compound with sodic chloride, and by yielding lactonic and mucic acids as its first products of oxidation, in this resembling dulcite, which latter can be obtained from it by addition of hydrogen. Lactose is therefore the first aldehyde of dulcite.

Non-fermentable Sugars of the Formula $C_6H_{12}O_6$.

875. *Inosite*, $C_6H_{12}O_6,2H_2O$, is contained in small quantity in the juices of animal muscle (especially those of the heart) and numerous organs, and also occurs in the urine during some diseases of the kidney.

To obtain it the mother liquor of the creatine crystals (§ 727) is acidulated with sulphuric acid and then gradually mixed with alcohol. Potassic sulphate first separates, and later inosite in cauliflower-like groups of colourless crystals, which on recrystallisation separate in large rhombic prisms of sweet taste. It effloresces in air, losing its water of crystallisation, and then melts at 210°. It dissolves in 16 parts of water at 10·5°, is insoluble in absolute alcohol and ether.

On dissolving inosite in strong nitric acid and then adding concentrated sulphuric acid, nitroïnosite separates. This appears to have the composition $C_6H_6(O.NO_2)_6$. Therefore inosite is not an aldehyde sugar, but a hexhydric alcohol of the formula $C_6H_6(OH)_6$.

A very characteristic rose coloration is obtained by evaporating inosite nearly to dryness with nitric acid, adding some solution of ammoniacal calcic chloride and once more evaporating.

Mercuric nitrate gives a yellow precipitate with solutions of inosite, which, on heating, turns red and serves as a means of detecting inosite.

Inosite is also found in many plants, especially in green beans, the shells of peas, in the unripe berries and leaves of the vine, in asparagus, &c.

Sorbin, $C_6H_{12}O_6$, occurs in mountain ash berries, and forms large colourless crystals, readily soluble; on oxidation it first yields aposorbic acid.

Arabinose, or *gum sugar*, $C_6H_{12}O_6$, is formed, together with a fermentable syrupy sugar, by the decomposition of arabin by dilute boiling sulphuric acid. It crystallises in large transparent rhombic prisms, readily dissolving in water and melting at 160°. The solution is strongly dextrorotary ($a = +116°$), has an intensely sweet taste, and reduces alkaline cupric solutions to cuprous oxide and silver solutions to metal.

Eucaline, $C_6H_{12}O_6$ (after drying at 100°), is formed, together with dextrose, by the decomposition of melitose (see § 881). It is an amorphous, dextrorotary mass, which is readily decomposed on heating, reduces alkaline cupric solutions, and is oxidised to oxalic acid by nitric acid.

876. *Sugars from Caoutchouc.*—Commercial caoutchouc contains several peculiar methyl-ether saccharine bodies. They are obtained by heating the finely divided caoutchouc with alcohol, and are left in the crystalline form on evaporation of the solvent. By heating with hydro-haloids they yield methyl haloid and non-fermentable sugars of the formula $C_6H_{12}O_6$.

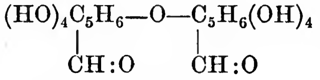
Two may be mentioned as representative.

Dambonite, $C_8H_{16}O_6 = C_6H_{10}(CH_3)_2O_6$, is obtained in the abovementioned way from the caoutchouc of Gaboon. It crystallises in prisms, which melt at 190° and sublime slowly at 210°. On heating with concentrated hydrochloric acid to 110°, methylic chloride and *dambose*, $C_6H_{12}O_6$, are obtained. The latter crystallises in thick six-sided prisms, melting at 212°; it is pretty soluble in water, but insoluble in alcohol.

Borneo caoutchouc yields *bornesite*, $C_7H_{14}O_6 = C_6H_{11}(CH_3)O_6$, crystallising in rhombic prisms, melting at 175°, and decomposed by hydriodic acid into methylic iodide and *Borneo dambose*, $C_6H_{12}O_6$, which melts at 220°.

Sugars, $C_{12}H_{22}O_{11}$. *Saccharoses.*

877. All these sugars, on boiling with dilute acid or by action of ferments on aqueous solutions, take up water, and are converted into two molecules of the formula $C_6H_{12}O_6$. They must therefore be anhydrides of the latter (corresponding to the dialkyl oxides), and have the general formula:



$$\begin{array}{ccc}(HO)_4C_5H_6 & —O— & C_5H_6(OH)_4 \\ | & & | \\ CH{:}O & & CH{:}O\end{array}$$

when derived from the aldehyde sugars.

Numerous cases of isomerism are possible both where two different aldehyde sugars are united or where two molecules of the same combine.

The decomposition by boiling with dilute acids—termed *inversion*—leads in every case to the formation of a saline compound as an intermediate product.

$$[C_6H_7O(OH)_4]_2O + H_2SO_4 = C_6H_7O(OH)_4(O.SO_2.OH) \\ + C_6H_7O(OH)_5,$$

from which, by boiling with water, regeneration of the acid is effected:

$$C_6H_7O(OH)_4(O.SO_2.OH) + H_2O = C_6H_7O(OH)_5 + HO.SO_2\,OH,$$

the latter then repeating the process with fresh molecules of the anhydride sugar.

The sugars $C_{12}H_{22}O_{11}$ are not directly fermentable, but when treated with yeast are mostly inverted, and then converted into alcohol and carbonic anhydride.

Cane Sugar, or Saccharose, $C_{12}H_{22}O_{11}$.

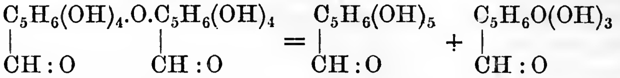
878. Cane sugar occurs in small quantity in nearly all sweet fruits, richly in the sugar cane and in *sorghum*, many roots, the sugar maple, and in the liquid contained in the nectaries of flowers.

To prepare cane sugar the expressed juice of the plant is heated to 100° with 5 % of calcic hydrate in the form of milk of lime, in order to prevent the inverting action of free acids and to precipitate mucous and albuminoid bodies. To remove colouring matters the liquid is filtered through thick layers of bone charcoal, and the nearly colourless liquid is then evaporated in vacuo as quickly as possible, and at the lowest temperature, until on cooling a crystalline mass is obtained. The crystals are purified commercially by washing with a concentrated solution of sugar.

By slow evaporation of concentrated solutions saccharose separates in large colourless, monoclinic crystals (sugar candy).

The taste of cane sugar is extremely sweet. It dissolves in one-third of its weight of cold water to a colourless syrup, and is strongly dextrorotary ($[\alpha] = + 73°–74°$). It is nearly insoluble in absolute alcohol.

It melts at 160° and solidifies on cooling to a glassy, hygroscopic mass (barley sugar), which in concentrated aqueous solution is slowly transformed into crystalline saccharose. If the melted sugar is kept for a long time at 160° it is decomposed, without loss of weight, into dextrose and lævulosane :



$$\begin{array}{llclcl}
C_5H_6(OH)_4.O. & C_5H_6(OH)_4 & & C_5H_6(OH)_5 & & C_5H_6O(OH)_3\\
| & | & = & | & + & |\\
CH:O & CH:O & & CH:O & & CH:O
\end{array}$$

At 200° it evolves water and is converted into *caramel*, a very bitter, strongly hygroscopic brown substance, which does not combine with water to form sugar. It is a mixture of different substances, the main portion consisting of a body of the formula $C_{12}H_{18}O_9$, or some multiple thereof.

On stronger heating sugar swells up and is completely decomposed. It evolves gases (CO_2, CO, CH_4, &c.) and vapours (H_2O, acetic acid, aldehyde, acetone, and oils), and leaves a residue of charcoal.

On mixing saccharose with concentrated sulphuric acid it is converted, with evolution of much formic acid and sulphurous anhydride, into a black charred mass; other mineral acids act in a similar way. When dilute they, as do also strong organic acids, produce inversion, i.e. decompose the saccharose into a mixture of equal molecules of dextrose and lævulose. Most ferments produce the same change in the first stage of their action. The mixture of the two aldehyde sugars is termed *invert sugar*. It rotates the plane of polarisation to the left, the lævorotary power of lævulose in solution (− 104°) considerably exceeding the dextrorotary power of dissolved dextrose (+ 56°). Honey is the saccharose of the nectaries of flowers, inverted by a ferment in the body of the bee.

On heating saccharose with manganic oxide and dilute sulphuric acid it yields much formic acid; with nitric acid it yields first saccharic acid, which is further oxidised to tartaric acid, and finally, on long heating with nitric acid, converted into oxalic acid.

879. *Metallic Compounds of Cane Sugar.*—Like all polyhydric alcohols, cane sugar, on contact with metallic oxides, can exchange a portion of its hydrogen for metal. These compounds behave like those of dextrose, are of basic reaction, and are decomposed by carbonic anhydride.

Alcoholic solutions of saccharose and potassic hydrate give a precipitate of *potassium saccharose*, $C_{12}H_{21}KO_{11}$.

On mixing milk of lime with much sugar solution and adding alcohol a precipitate of *calcium saccharose*, $C_{12}H_{20}CaO_{11},H_2O$, is obtained. By boiling an aqueous solution saturated with lime *tricalcium saccharose*, $C_{12}H_{16}Ca_3O_{11},3H_2O$, precipitates as an amorphous powder. On mixing a solution of saccharose with plumbic acetate and carefully adding ammonia, a precipitate, at first amorphous, but soon becoming crystalline, is obtained of the formula:

$$C_{12}H_{20}Pb_2O_{11},H_2O.$$

In presence of alkalies it dissolves cupric oxide, forming a blue solution, from which cuprous oxide precipitates slowly on boiling.

Cane sugar gives difficultly a crystallisable compound with sodic chloride, $C_{12}H_{22}O_{11},NaCl$ (as also with similar salts), which tastes at once sweet and saline and is the cause of considerable loss of sugar in its preparation from beet-root.

Saccharose Salts.—In accordance with the formula:

$$[C_6H_7O(OH)_4]_2O,$$

eight hydrogen atoms can be replaced in cane sugar on heating with organic anhydrides. Acetic anhydride gives *saccharose octacetate*, $C_{12}H_{14}(C_2H_3O_2)_8O_{11}$, as a white amorphous, insoluble mass, which on heating with water yields acetic acid, dextrose, and lævulose.

Milk Sugar, $C_{12}H_{22}O_{11},H_2O$.

880. Milk sugar occurs only in the milk of the mammalia, and is obtained by precipitating the casein and fats with dilute acids, evaporating the whey to a thin syrup, and long standing in a cool place, when it crystallises out. It forms hard, colourless, transparent four-sided prisms, of feebly sweet taste, only dissolving slowly in cold water, requiring of the latter 6 parts, of boiling water $2\frac{1}{2}$ parts, for solution. The solution is dextrorotatory ($[a] = +59{\cdot}3°$). It is insoluble in ether and alcohol. The water of crystallisation is given off at 130°, but is regained on solution.

At 170°–180° milk sugar is converted with loss of water into lacto-caramel, $C_{12}H_{20}O_{10}$, an amorphous brown powder, which cannot be reconverted into milk sugar by water, and melts with decomposition at somewhat above 200°.

Milk sugar reduces argentic oxide to metal, and alkaline cupric solutions to cuprous oxide. With basic hydrates it yields metallic compounds of alkaline reaction, decomposed by carbonic anhydride. By boiling with dilute acids, or by ferments, it is split up into *lactose* and a body which appears to be dextrose. In consequence of this it enters into the alcoholic fermentation with yeast and gives lactic acid with putrefaction ferments.

Bromine and water oxidise it to lactonic acid, nitric acid to mucic acid (from the lactose) and saccharic acid (from the dextrose), both of which are further converted into tartaric and oxalic acids.

By heating with acetic anhydride the octacetate:

$$C_{12}H_{14}(O.C_2H_3O)_8O_{11},$$

is obtained.

881. *Melizitose*, $C_{12}H_{22}O_{11},H_2O$, occurs in the manna of Briançon, an exudation from the young shoots of the larch (*Larix europaea*), and is obtained therefrom by extraction with alcohol and crystallisation. It forms small, hard, brilliant crystals, which dissolve in little water and have a very sweet taste. The solution is more strongly dextrorotary than cane sugar. Boiling dilute acids invert melizitose, converting it into dextrose.

Melitose, $C_{12}H_{22}O_{11},3H_2O$, the chief constituent of Australian eucalyptus manna, crystallises in fine interlaced needles, of weak, sweet taste, whose solution is dextrorotary. Alkaline cupric solutions are not reduced by melitose. Dilute acids and ferments invert it into a mixture of dextrose and eucalyne. On fermenting a solution of melitose with yeast and evaporation of the liquid, eucalyne is left unaltered.

Synanthrose, $C_{12}H_{22}O_{11}$, is found in the tubercules of several of the compositæ, e.g. of *Dahlia variabilis* and *Helianthus tuberosus,* together with inulin. It is amorphous and deliquescent. On inversion it yields lævulose together with another sugar not yet sufficiently characterised.

881*a*. *Maltose,* $C_{12}H_{22}O_{11}$, is obtained, together with dextrin, by heating starch with dilute acids, or by the action of diastase, the filtrate being then evaporated, the resulting syrup extracted with boiling alcohol, and the alcoholic solution allowed to stand for some days, when maltose crystallises out in hard crusts of fine needles of $C_{12}H_{22}O_{11},H_2O$. The specific rotary power for the anhydrous body $[a]_j = +150°$. Two molecules of maltose reduce 6·5 molecules of CuO. It is capable of inversion; the resulting dextroses require further investigation.

Carbo-hydrates of the Formula $(C_6H_{10}O_5)_x$.

882. The compounds of this group appear to be the second anhydrides of the aldehyde sugars, $C_6H_{12}O_6$; they differ from the isomeric bodies obtained from the latter by heating the latter (glucosan, lævulosan, &c.), in all probability by having a greater molecular weight. How many simple groups $C_6H_{10}O_5$ are combined together by oxygen to form the molecule has not yet been determined. Many of them seem, according to the analysis of their saline derivatives, to be triply polymeric. Some are converted by ferments, and all—even the insoluble—by boiling with dilute sulphuric acid into sugars of the formula $C_6H_{12}O_6$, the sulphuric acid playing the same part as in the inversion of cane sugar (§ 877).

So far research seems to have shown that the members of the group contain three replaceable hydrogen atoms for each six carbon atoms, so that the sugar radical must be united with four anhydrous oxygen bonds and three hydroxyl groups.

They are without exception destitute of taste and smell.

Cellulose, $(C_6H_{10}O_5)_x$.

883. The walls of vegetable cells all contain *cellulose* as their essential groundwork. Differences of chemical behaviour, which essentially shrink to difference in the ease with which they suffer change, depend probably only on the greater or less state of aggregation, also partly on admixture with, or actual envelopment by, other bodies.

This latter occurs in the woody parts of vegetables, so that for a time another body in close relationship to cellulose, and termed lignine, was supposed to exist.

In the pure state cellulose is most readily isolated from young and tender portions of vegetables, these being divided as finely as possible in order to rupture the cells, and then extracted with dilute hydrochloric acid, water, alcohol, and ether, until none of these solvents remove anything more. Fine filter paper or cotton wool yield pretty pure cellulose by similar treatment.

Cellulose is a colourless, transparent mass, absolutely insoluble in water, alcohol, or ether, which self-evidently must still possess the original organic structure. It is dissolved without great chemical change by an aqueous cuprammonic solution, prepared from basic carbonate or hydrate of copper and aqueous ammonia. It is but little dissolved by the cuprammonic salts of strong acids.

On over-saturating such a solution with dilute hydrochloric acid cellulose is precipitated unchanged in white flocks.

In cold concentrated sulphuric acid cellulose at first swells up. If, when all converted into a paste-like mass, it be poured into a large quantity of water, colourless flocks of the formula $(C_6H_{10}O_5)_x$ separate, but these differ essentially from cellulose, as, like starch, they are coloured *blue* by iodine. This body has been termed *amyloid*. In preparing 'parchment paper,' filter paper is dipped for a few seconds into a cold mixture of one part of water and two parts sulphuric acid, whereby the surface is converted into amyloid; the paper is then washed with much water and finally with dilute aqueous ammonia.

Cellulose is completely dissolved on long standing in concentrated sulphuric acid. If the action be continued until water no longer produces a precipitate, the cellulose is converted into dextrin, which, on boiling the acid solution, will be converted into dextrose.

If cellulose be heated to 200° with potassic hydrate and a little water, it yields hydrogen, methylic alcohol, and potassic carbonate, oxalate, acetate, and propionate.

884. *Cellulose Salts. Cellulose Nitrate.*—If cellulose in the most finely divided condition, as pure cotton wool, be dipped into a mixture of concentrated sulphuric and nitric acids, it is converted without change of form into nitrate. The more or less complete replacement of hydroxylic hydrogen by nitryl (NO_2) depends partly on the concentration of the nitric acid, partly on the duration of the action. If the most concentrated nitric acid be employed with not too much sulphuric acid, and the cotton wool allowed to remain in contact for some time, there is then obtained, after careful washing with water, the so-called *trinitro-cellulose*, $[C_6H_7O_2(O.NO_2)_3]_x$, which immediately burns on contact with glowing bodies. It is completely insoluble in water, alcohol, and ether, and is reconverted into cellulose by the long-continued action of bodies which yield nascent hydrogen (such as acetic acid and iron), or by an acid solution of ferric chloride, the nitrogen being evolved as ammonia in the first case and as nitric oxide in the second.

By a shorter duration of the action or by employment of nitric acid either not quite concentrated or mixed with much sulphuric acid, a less nitrated product is obtained, which burns explosively. To prepare '*gun cotton*' (pyroxylin), cotton wool purified by washing with water and weak sodic hydrate, and subsequently dried, is dipped for a few minutes (about five) in a mixture of one volume of concentrated sulphuric acid and two volumes of concentrated nitric acid, washed with water till of neutral reaction, and dried at the ordinary temperature. The explosive force of gun cotton is about four times that of an equal quantity of gunpowder.

If, instead of cold, a warm nitration mixture be employed, or if a large quantity of sulphuric acid be added to the first, and the cotton left in contact with it for some time, the resulting nitrate is then soluble in a mixture of one part of alcohol and four parts of ether to a syrupy liquid, '*collodion.*' On evaporation in air the nitro-cellulose is left as a transparent, waterproof membrane. Collodion, therefore, finds much use in surgery and in the preparation of photographic negatives on glass.

If finely divided cellulose be heated to 180° in a sealed glass tube with six to eight times its weight of acetic anhydride, a syrupy solution of *triacetyl cellulose* in acetic acid is obtained, from which the compound $[C_6H_7O_2(O.C_2H_3O)_3]_x$ can be separated by water in the form of white flocks insoluble in alcohol or ether.

885. *Tunicine*, or *animal cellulose*, is isomeric with cellulose, and closely resembles it in chemical character. It is obtained from the mantles of ascidians and cyntheans by long boiling with hydrochloric acid and sodic hydrate, followed by washing with water, alcohol, and ether. It is not attacked by dilute sulphuric acid even on long boiling, but gives dextrose by dissolving in cold concentrated sulphuric acid and pouring into water.

Starch, or Amylum, $(C_6H_{10}O_5)_3$ (?).

886. Starch occurs most widely disseminated in the vegetable kingdom, always in the form of microscopic granules enclosed in the vegetable cells. It occurs in seeds (corn, chestnuts) in the trunk, especially in many palms, in roots (of *Jatropha Manihot* as tapioca, of *Maranta arundinacea* as arrowroot in commerce), in tubers (potato), &c. To prepare it the vegetable is finely ground, so as to tear the cell membranes, the starch washed with water, and the milky liquid, after passing through a fine sieve, allowed to stand quietly for some time, when the starch settles to the bottom of the vessel.

From the meal of grain, especially of wheat, it is best obtained by allowing the meal to remain for a long time in contact with water, when the nitrogenous constituents (gluten, &c.) enter into putrefaction and go in great part into solution, whilst the starch remains unchanged and can be purified by washing, &c. It is finally dried in air at the ordinary temperature.

Starch granules possess very different sizes (e.g. ·185 mm. long in potato starch and ·045 mm. in wheat starch), and, as a rule, show under the microscope a series of concentric markings, of which the innermost nucleus (the hilium) appears to lie at one side. In polarised light starch granules (like the sections of many crystals) show a dark cross, whose point of intersection agrees with the hilium.

The integument of the starch granule, and also of the small layers, appears to consist of a very brittle layer of cellulose.

In mass starch forms a glittering white powder, insoluble in cold water, and from which alcohol and ether remove minute quantities of wax-like and fatty substances. In water heated to more than 60° the contents of the granules swell, break the integument, and soon diffusing through the whole of the hot liquid, make the mass appear like a solution. On cooling, if too much water has not been employed, it becomes a transparent jelly, termed *starch paste*, and dries to a hard transparent mass.

The most characteristic reaction for starch, both as granules and as paste, is the deep blue colour which it gives with iodine. The combination between the two is very feeble; it decomposes with loss of colour on heating, but the colour returns on cooling.

On mixing boiling solutions of starch with lime or baryta water, or with basic plumbic acetate, white precipitates are obtained of metallic derivatives of starch.

On long boiling starch paste loses the power of gelatinising on cooling, having been converted into a modification soluble also in cold water, which is strongly dextrorotary, is precipitated by alcohol, and gives a blue coloration with iodine.

The same conversion into *soluble starch* is effected by long heating to 100° in the dry state, or by gentle heating with solutions of diastase (the ferment of germinating grain), zincic chloride, or dilute sulphuric acid, but soon passes first into maltose and dextrine, and finally into dextrose (comp. § 870). If dry starch be heated to 200° it is converted into dextrin.

On boiling with nitric acid starch yields the same oxidation products as dextrose.

Starch dissolves readily in cold concentrated nitric acid; on diluting largely with water a white powder, *xyloidine*, separates. This is a nitrate of the formula $C_6H_9(NO_2)O_5$ or $[C_6H_7O_2(O.NO_2)(OH_2)_2]_x$, which, after washing and drying, inflames at 180° and burns briskly, leaving some charcoal. If the nitric acid solution be mixed with sulphuric acid, there is then obtained, on dilution with water, a similar white powder of a higher nitrate, which has approximately the formula $C_6H_8(NO_2)_2O_5$ or $[C_6H_7O_2(O.NO_2)_2OH]_x$.

By heating starch to 140° with much acetic anhydride *triacetyl amylum*, $[C_6H_7O_2(O.C_2H_3O)_3]$, is obtained as an amorphous mass, insoluble in water, alcohol, and acetic acid; with dilute alkalies it gives starch and acetates.

Paramylum occurs in the green infusoria *Euglena viridis* in granules, the mass closely resembling starch; it is insoluble in cold water and dilute acids, swells up in hot water, and is converted into a fermentable sugar by hot hydrochloric acid.

887. *Lichenine*, or *moss starch*, $xC_6H_{10}O_5$, occurs in many lichens, especially in Iceland moss. Finely divided Iceland moss is washed with alcohol, ether, weak solution of sodic hydrate, dilute hydrochloric acid, and finally with water, and the lichenine then extracted with boiling water. The clear hot solution becomes a colourless jelly on cooling, which after drying forms a hard transparent mass. Iodine gives with lichenine a yellow or brown colour, frequently, however, probably from the presence of some starch, a green or faint blue colour. On boiling with dilute acid lichenine is converted into a fermentable sugar.

Inuline, $xC_6H_{10}O_5$, occurs in the roots of many compositæ—e.g. in

Inula Helenium, *Helianthus tuberosus*, *Leontodon Taraxacum*, and especially in the tubercules of the dahlia. It is obtained either like starch or by boiling with water, from which it precipitates on cooling as a white powder. It is nearly insoluble in cold water, but is largely dissolved on boiling. Its solution is lævorotary, and on inversion with dilute sulphuric acid gives *lævulose*. It is coloured yellow by iodine.

888. *Glycogen*, $xC_6H_{10}O_5$, occurs in the animal liver in largest quantity during and shortly after digestion, and has also been recognised in the fœtus during the first month of its existence, in yolk of eggs, and in many mollusca. It vanishes from the liver with extraordinary rapidity after death, being converted into sugar by the ferment of that organ.

To prepare it animals are killed quickly whilst in the full act of digestion, the liver removed, coarsely divided, rubbed to a pulp with sand heated to 100°, and then extracted several times with hot boiling water. The filtered opalescent solution is treated with alcohol, which precipitates impure glycogen; the precipitate is boiled with concentrated potassic hydrate as long as ammonia is evolved, in order to destroy admixed albuminoids, and after large dilution again precipitated with alcohol. The glycogen is then repeatedly dissolved in acetic acid and precipitated with alcohol, finally washed with absolute ether, and dried in vacuo.

It is a white amorphous powder, destitute of smell or taste, which gives an opalescent solution with water, and is coloured wine red by iodine. It is very readily converted into dextrose by dilute acids, &c.

Dextrin, $xC_6H_{10}O_5$.

889. As already mentioned, starch is converted into dextrin by the action of dilute acids, of diastase, or by heating to 200°. In preparing it commercially the starch is moistened with water containing about 2 % of nitric acid, allowed to dry in air, and the conversion finally effected by heating to 110°.

The crude dextrin so prepared is a clear yellow powder, from which the pure compound can be obtained by solution in water and precipitation of the filtrate by alcohol. It dissolves largely in water to a gummy, slimy mass, which leaves a transparent, gum-like mass on evaporation and drying. The aqueous solution is strongly dextrorotary ($[\alpha] = +138{\cdot}5°$), is not blued by iodine, does not reduce alkaline cupric solutions even on boiling, and is finally completely converted into grape sugar by dilute acids and diastase.

On heating dextrin with an excess of acetic anhydride it yields *triacetyl dextrin*, $xC_6H_7(C_2H_3O)_3O_5$, which can also be obtained from the isomeric triacetyl amylum at 160°. It is amorphous, insoluble in water and alcohol, but soluble in acetic acid.

Gums and Mucilages, $xC_6H_{10}O_5$.

890. Under these names a number of different but closely related bodies are collected, which are widely disseminated in plants; they are partly readily soluble in water (gums), partly only swell up therein (mucilage). The gums occur dissolved in the juices of plants, but exude on rupture of the cells, and harden in the air to a transparent mass of vitreous fracture. The natural gums and mucilages are invariably metallic derivatives of peculiar organic compounds, and therefore leave a relatively large quantity of ash, consisting of the carbonates of potassium, calcium, and magnesium.

Arabin is the organic constituent of gum arabic, an exudation on different tropical acacias. In these it occurs mainly as the calcic compound. It is obtained from gum arabic by solution in water, acidulation with hydrochloric or acetic acids, and addition of alcohol, when it precipitates in flocks. By frequent repetition of this process it is obtained free from metal, and can no longer be precipitated from its aqueous solution by addition of alcohol, but again acquires that property on addition of small quantities of basic hydrates or inorganic salts.

After drying at 100° it is a glassy mass of conchoidal fracture and a composition corresponding to the formula:

$$C_{12}H_{22}O_{11} \text{ or } C_{12}H_{20}O_{10},H_2O,$$

which decomposes carbonates, yielding compounds containing 1 equivalent of metal to 18 atoms of carbon. Probably, therefore, the molecular formula of arabin dried at 100° should be $C_{36}H_{66}O_{33}$.

At 120°–130° arabin loses weight until it has the composition $nC_6H_{10}O_5$ ($C_{36}H_{60}O_{30}$ or $C_{18}H_{30}O_{15}$?). It is then insoluble in water, but swells up enormously in it (*metarabin*). By addition of potassic hydrate solution or lime water it forms the metallic derivatives of ordinary arabin.

Compounds of arabin with potassium and calcium form the main portion of cherry and plum tree gums, and occur frequently in other plants, e.g. sugar beet.

All solutions of arabin and its metallic derivatives rotate the plane of polarisation, but to very different degrees, and are in part dextro-, in part lævo-rotary. By boiling with dilute sulphuric acid they are all without exception converted into a dextrorotary mixture of partly fermentable sugars, in which arabinose (§ 294) always occurs.

Bassorin.—This name was first given to the chief constituent of Bassora gum, which is obtained from a species of cactus. This drug is insoluble in water, but swells up therein to a slimy jelly. Later the name was extended to all vegetable substances of similar nature, which in their totality are termed *vegetable mucilages.* These occur in the roots of different orchis (salap), in the roots of althæa, quince kernels, *Semen Psylii,* Carraghen moss, &c., as a rule mixed with gum. Mucilages also occur in cherry and plum tree gums, and in *traganth,* the hardened juice of some kinds of *Astragalus.*

Gum or bassorin-like bodies are formed, together with butyric acid and mannite, in the mucous fermentation of sugar.

On heating with nitric acid, gums and mucilage yield much mucic acid and also saccharic acid; as products of further oxidation, tartaric and oxalic acids.

Pectous Substances.

891. Under this name are included a series of bodies which are most widely disseminated in plants, especially in fleshy fruits and roots, which further stand in very clear relation to the carbo-hydrates, and always occur together with gum and mucilage. The chemistry of these compounds is still very obscure.

A completely insoluble body, *pectose*, occurs in unripe fleshy fruits and roots, and is converted on ripening or by long boiling into bodies dissolving in water, or in part apparently dissolving and gelatinising on cooling. The products distinguished as pectine, parapectine, metapectine, pectoic acid, pectic acid, and parapectic acid are not sufficiently individualised to require further notice here. The end product of all these metamorphoses, the body termed metapectic acid, has lately been shown to be slightly impure arabine.

PYRIDINE BASES, $C_nH_{2n-5}N$.

892. The group of pyridine bases appears also to belong to the derivatives of the heptavalent hydrocarbon nucleus, C_nH_{2n-5}. They were first obtained in inconsiderable quantity from the oily products of the dry distillation of nitrogenous organic matter, such as turf, coal, and bones. From bone oil they were obtained by shaking with dilute hydrochloric acid, when they go into aqueous solution as hydrochlorides, from which they are separated, together with alkylamines, such as trimethylamine, butylamine, and amylamine, on addition of alkali. The separation of the single homologues from one another is very difficult and tedious. Latterly several of them have been obtained from well-known compounds of other groups.

The structure of these compounds is yet but little known; they appear, however, to belong to the nitril bases, as ethylic iodide unites with them, giving iodides of ammonium radicals, from which the base cannot be separated by alkali, whilst argentic oxides convert the iodide into strongly alkaline bases, corresponding to the tetralkylammonic hydrates.

Pyridine, C_5H_5N, is obtained in small quantity amongst the products of the action of phosphoric anhydride on isoamylic nitrate:

$$C_5H_{11}.O.NO_2 + 3P_2O_5 = 6HPO_3 + C_5H_5N.$$

It is a colourless liquid of sharp, nauseous odour, boiling at 116·5°, and has sp. gr. ·986 at 0°. It yields a deliquescent salt with hydrochloric acid of the formula $C_5H_5N.HCl$, whose yellow platinochloride, $(C_5H_5N.HCl)_2PtCl_4$, is difficultly soluble in water.

On long treatment with metallic sodium, especially on heating, it polymerises to solid *dipyridine*, melting at 108°, crystallising in needles, and is sublimable.

Picoline, C_6H_7N, can be obtained by the dry distillation of acroleïn ammonia (§ 763):

$$C_6H_9NO = H_2O + C_6H_7N,$$

and by heating glyceryl tribromide (§ 681) to 250° with alcoholic ammonia. It is a liquid, is strongly basic and closely resembles pyridine, is soluble in water, boils at 135°, has sp. gr. ·961 at 0°, and is polymerised by sodium.

Lutidine, C_7H_9N, has only been obtained from tar oil. It boils at about 155° and has sp. gr. ·946 at 0°.

Collidine, $C_8H_{11}N$, is formed from aldehyde ammonia by dry distillation or by heating the alcoholic solution to 120°–130°; it is also obtained from oxytetraldine (§ 424):

$$C_8H_{13}NO = H_2O + C_8H_{11}N.$$

Ethylidene dichloride is also converted into collidine by ammonia solution at 160°. It is a colourless liquid, little soluble in water, of sp. gr. ·944 and boiling point 179°.

The following higher homologues have been separated from coal tar, but have been little investigated: *parvoline* ($C_9H_{13}N_3$, boils at 188°), *corindine* ($C_{10}H_{15}N$, boils at 211°), *rubidine* ($C_{11}H_{17}N$, boils at 230°), and *viridine* ($C_{12}H_{19}N$, boils at 251°).

DERIVATIVES OF THE HYDROCARBON NUCLEUS, C_nH_{2n-6}.

MONOBASIC ACIDS.

893. *Mannitic acid*, $C_5H_6(OH)_5.CO.OH$, results, along with its aldehyde, mannitose (§ 873), when a concentrated aqueous solution of mannite is oxidised by platinum black. It is an amorphous, extremely soluble substance. It forms salts which contain mostly two equivalents of a metal, one equivalent probably replacing a hydroxylic hydrogen atom.

Gluconic acid, isomeric with the above, is obtained from grape sugar, or glucose, by oxidation with chlorine. The acid is a colourless syrup, and forms monobasic salts, mostly soluble with the exception of the calcium one. The acid is optically active.

894. *Lactonic acid*, $C_5H_6(OH)_3.CO.OH$, obtained by oxidation of arabin and milk sugar, is a deliquescent crystalline mass, melting at 100°. It seems to stand in the same relation to the previous acids that mannitan does to mannite and glucosan to grape sugar. It takes up two equivalents of metal from basic hydrates, but only one from carbonates.

DIBASIC UNSATURATED ACIDS, $C_nH_{2n-4}.O_4$, or $C_{n'}H_{2n'-2}(CO.OH)_2$.

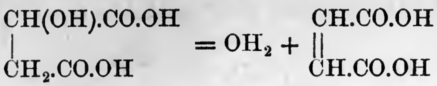
895. In this group is included with certainty only acids of the formulæ $C_4H_4O_4$ (fumaric and maleïc acids), $C_5H_6O_4$ (pyrocitric acids), and $C_6H_8O_4$ (hydromucic acids), to which the camphoric acids, $C_{10}H_{16}O_4$, may probably be added; but, as their constitution is less accurately known, they will be described later on under the oxidation products of the camphors.

As unsaturated compounds in whose hydrocarbon radical, C_nH_{2n-2}, a double connection of neighbouring carbon atoms takes place, they possess the power of combining directly with two atoms of a halogen, with the elements of a molecule of hydric haloid, or with two atoms of hydrogen. In the latter case acids of the series $C_nH_{2n}(CO.OH)_2$ result, or, by addition of halogens and their hydrides, mono- or di-substitution products or derivatives of the same.

Acids, $C_4H_4O_4$ *or* $C_2H_2(CO.OH)_2$.

896. 1. *Fumaric Acid.*—This acid exists on many plants—e.g. *fumitory* (*Fumaria officinalis*), Iceland moss, and several fungi.

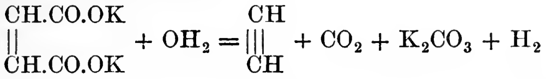
Artificially it may be conveniently obtained by heating malic acid for some time to 150°, until water ceases to distil over:



$$\begin{array}{l}CH(OH).CO.OH\\ |\\ CH_2.CO.OH\end{array} = OH_2 + \begin{array}{l}CH.CO.OH\\ \|\\ CH.CO.OH\end{array}$$

Malic acid may also be converted into fumaric by boiling with fuming HCl. Monobrom-succinic acid splits up at 160° into fumaric acid and hydric bromide.

Fumaric acid crystallises in small prisms, which cannot be fused without undergoing change. In cold water they are very difficultly soluble. Of its salts only those of the alkalies are easily soluble. The barium and calcium salts, $C_4H_2BaO_4$ and $C_4H_2CaO_4$, are difficultly soluble crystalline precipitates; the silver salt a perfectly insoluble amorphous powder, which explodes on heating. The alkaline salts yield acetylene on electrolysis:



$$\begin{array}{l}CH.CO.OK\\ \|\\ CH.CO.OK\end{array} + OH_2 = \begin{array}{l}CH\\ |||\\ CH\end{array} + CO_2 + K_2CO_3 + H_2$$

Ethylic fumarate, $C_2H_2(CO.O.C_2H_5)_2$, is obtained on distillation of ethylic malate and by saturating a solution of a mixture of fumaric acid and ethyl alcohol with hydric chloride, or still better by the action of ethylic iodide on argentic fumarate. It is a colourless oily liquid, boiling at 218°, which on contact with ammonia quickly passes into insoluble *fumaramide:*

$$C_2H_2(CO.NH_2)_2.$$

Fumaric acid distilled with phosphoric pentachloride gives *chlor fumaryl:*

$$C_2H_2(CO.OH)_2 + 2PCl_5 = 2POCl_3 + 2HCl + C_2H_2(CO.Cl)_2,$$

a liquid boiling at 160°, reproducing on contact with water fumaric acid and hydric chloride.

Fumaric acid combines directly with nascent hydrogen to form ordinary succinic acid, and with a molecule of bromine yielding dibrom-succinic acid.

2. *Maleïc Acid.*—This acid is formed in considerable quantity by the quick distillation of malic acid, and can also be produced from fumaric acid.

If the latter acid be distilled it splits up into water and an anhydride, $C_2H_2(CO)_2O$, which on again combining with water forms maleïc acid.

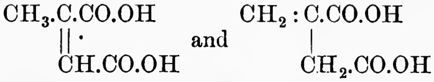
Maleïc acid is easily soluble in cold water and crystallises in colourless leafy crystals, melting at 130°; at 160° it breaks up into water and the anhydride. The acid, if fused and maintained for some time at about its fusing point, solidifies on cooling to fumaric acid; this change can also be effected by boiling with dilute sulphuric, hydrobromic, or hydriodic acids. Nascent hydrogen converts it into ordinary succinic acid, bromine into isodibrom-succinic acid. Its salts, including those with barium and calcium, are somewhat easily soluble in water. The neutral silver salt, $C_2H_2(CO.OAg)_2$, is at first amorphous, but crystallises after some time. An acid salt,

$C_2H_2(CO.OH.)(CO.OAg)$, forms colourless needles when a solution of the acid and argentic nitrate are mixed and allowed to stand for some days. By electrolysis salts of maleïc acid, like those of fumaric, yield acetylene.

Maleïc anhydride, $C_4H_2O_3 = C_2H_3{<}\begin{matrix}CO\\CO\end{matrix}{>}O$, obtained from fumaric or maleïc acid by repeated distillation, is a colourless crystalline mass, melting at 57° and boiling at 196°.

Acids, $C_5H_6O_4$ *or* $C_3H_4(CO.OH)_2$.

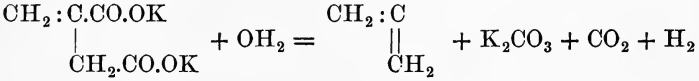
897. Three acids (itaconic, citraconic, mesaconic) of this formula are known isomeric with paraconic acid (§ 866). They are collectively obtainable from citric acid and may be termed generally *pyrocitric acids.* They are related to each other in constitution, somewhat similarly to fumaric to maleïc acids, giving, on distillation along with water, the same anhydride, $C_3H_4(CO)_2O$, which on again taking up the elements of a molecule of water gives citraconic acid; hence this anhydride is termed citraconic anhydride. All three acids combine with two atoms of nascent hydrogen and pass into pyrotartaric acid. As the structure of the latter (§ 838, 2) acid is known, only two formulæ are possible for the three pyrocitric acids:



$$\begin{array}{l}CH_3.C.CO.OH\\ \quad\ \ \|\\ \quad\ \ CH.CO.OH\end{array} \quad \text{and} \quad \begin{array}{l}CH_2:C.CO.OH\\ \qquad\ \ |\\ \qquad\ \ CH_2.CO.OH\end{array}$$

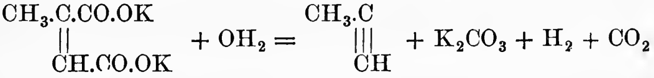
so that one of them must represent at least two acids.

Recent experiments have shown that salts of itaconic acid on electrolysis yield isallylene. The formulæ of itaconic acid must be therefore:



$$\begin{array}{l}CH_2:C.CO.OK\\ \quad |\\ \quad CH_2.CO.OK\end{array} + OH_2 = \begin{array}{l}CH_2:C\\ \qquad \|\\ \qquad CH_2\end{array} + K_2CO_3 + CO_2 + H_2$$

Citraconic and mesaconic acids, however, give allylene, and therefore both are represented by the first of the above formulæ:



$$\begin{array}{l}CH_3.C.CO.OK\\ \qquad \|\\ \qquad CH.CO.OK\end{array} + OH_2 = \begin{array}{l}CH_3.C\\ \qquad |||\\ \qquad CH\end{array} + K_2CO_3 + H_2 + CO_2$$

The first step in their preparation consists in the dry distillation of citric acid, whereby water is split off and aconic acid results:

$$C_3H_4(OH)(CO.OH)_3 = OH_2 + C_3H_3(CO.OH)_3,$$

which decomposes further into CO_2 and itaconic acid:

$$C_3H_3(CO.OH)_3 = CO_2 + C_3H_4(CO.OH)_2,$$

the latter acid being at the same time partially further decomposed into water and citraconic anhydride. The well-cooled distillate divides itself into an upper oily and a lower aqueous layer, from both of which, on cooling, itaconic acid crystallises out. The portion of the oily layer remaining liquid is mostly citraconic anhydride, whilst the watery portion is a solution of the easily soluble citraconic acid.

1. *Itaconic acid* may be also formed by heating citric acid with water to 160°. It crystallises in rhombic prisms, soluble at 10° in

17 parts of water and melting at 161°. It combines with hydric haloids to itahaloid pyrotartaric acids (§ 866, 1).

Its salts are mostly pretty easily soluble, the lead and silver salts difficultly so. *Ethylic itaconate*, $C_3H_4(CO.O.C_2H_5)_2$, boils at 227°.

2. *Citraconic acid* forms large shining four-sided prisms, which dissolve in less than their equal weight of water and melt at 80°. At 100°, or more quickly by heating a concentrated solution to 120°, it is changed into itaconic acid. Hydric chloride forms with it the very unstable citrachlor-pyrotartaric acid.

3. *Mesaconic acid* is produced by long heating of citraconic acid with dilute nitric or strong hydric chloride or iodide. Mesaconic acid crystallises in fine shining needles, which dissolve in 37 parts of water at 18° and melt at 208°. It combines with hydric chloride to form mesachlor-pyrotartaric acid, and splits up by dry distillation into citraconic anhydride and water.

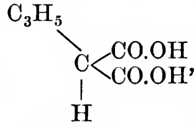
Citraconic anhydride, $C_3H_4{<}\begin{smallmatrix}CO\\CO\end{smallmatrix}{>}O$, is an oil boiling at 212°, which gives with PCl_5 *chlor-citraconyl*, $C_3H_4(CO.Cl)_2$, an oily body boiling at 175°.

898. 1. *Hydromuconic acid*, $C_6H_8O_4 = C_4H_6(CO.OH)_2$, is derived from mucic acid by the action of sodium amalgam on the dichloride (see *mucic acid*):

$$C_4H_2Cl_2(CO.OH)_2 + 6Na + 2OH_2 = C_4H_6(CO.ONa)_2 \\ + 2NaCl + 2NaOH.$$

It forms long prisms, difficultly soluble in water and melting at 195°, which by further addition of hydrogen passes into adipic acid (§ 839) and takes up two atoms of bromine to form dibrom adipic acid.

2. *Allyl malonic acid*,



$$\begin{array}{l} C_3H_5 \\ \quad\diagdown \\ \quad C{<}\begin{smallmatrix}CO.OH\\CO.OH\end{smallmatrix} \\ \quad | \\ \quad H \end{array}$$

prepared from ethylic allyl-malonate, is isomeric with the above acid and melts at 103°.

3. *Xeronic acid*, $\begin{array}{l} CH_2.C(CH_3).CO.OH \\ |\quad\ \ | \\ CH_2.C(CH_3).CO.OH \end{array}$, is contained in the distillate from citraconic anhydride, and may be separated by distilling the mixture of anhydrides with steam, when xeronic anhydride passes over. It boils at 242° and is liquid at −18°. The acid does not appear to exist in a free state, but salts are known.

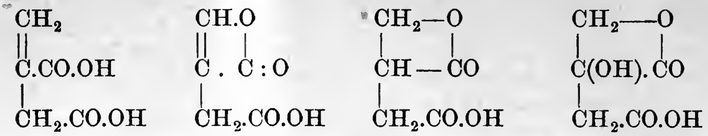
The acid is polymeric with methyl acrylic acid, to which it probably stands in the following relation:

$$\begin{array}{l} CH_2.C(CH_3).CO.OH \\ |\quad\ \ | \\ CH_2.C(CH_3).CO.OH \end{array} \quad \text{xeronic acid}$$

$$\begin{array}{l} CH_2.C(CH_3).CO\diagdown \\ |\quad\ \ | \qquad\qquad\quad >O \\ CH_2.C(CH_3).CO\diagup \end{array} \quad \text{xeronic anhydride}$$

$$\begin{array}{l} CH_2 \\ \| \\ C(CH_3).CO.OH \end{array} \quad \text{methyl acrylic acid}$$

The relations of itaconic acid to aconic, paraconic, and hydroxy-paraconic acids are shown by the formulæ:



Itaconic acid. Aconic acid. Paraconic acid. Hydroxy-paraconic acid.

DIBASIC SATURATED ACIDS.

899. The unsaturated acids of the previous group combine with two atoms of chlorine or bromine to form dihaloids, and hence appear as disubstituted products of members of the series $C_nH_{2n}(CO.OH)_2$, and can indeed be partly obtained from the latter by the action of Cl or Br.

In many of these the halogen atoms may be replaced by hydroxyl, producing dihydroxy-acids, $C_nH_{2n-2}(OH)_2(CO.OH)_2$, the most important representative of which is *tartaric acid.*

The unsaturated acids also combine with hypochlorous acid to form hydroxyl haloids, $C_nH_{2n-2}.Cl(OH)(CO.OH)_2$.

899*a*. *Dibrom-malonic acid,* $CBr_2:(CO.OH)_2$, crystallises in needles and melts at 127°.

Compounds of the Tartaric Acid Radical.

900. *Dibrom-Succinic Acids.*—Fumaric and maleïc acids combine when gently heated with two atoms of bromine, and, retaining their isomeric difference, yield two *dibrom-succinic acids.*

The ordinary *dibrom-succinic acid,* $\begin{array}{l}CHBr.CO.OH\\ |\\ CHBr.CO.OH\end{array}$, is *fumaric acid dibromide,* but can also be directly obtained from succinic acid by heating in sealed tubes with water and bromine to 150°. It forms crystals difficultly soluble in cold water, which on heating decompose completely without previous fusion. It is not affected by boiling water.

Chlor-fumaryl (§ 896) combines directly with bromine, forming *dibrom-succinyl dichloride,* $C_2H_2Br_2(CO.Cl)_2$, which boils between 218°–220° and gives, with alcohol, crystalline ethylic dibrom-succinate:

$$C_2H_2Br_2(CO.O.C_2H_5)_2.$$

Isodibrom-succinic acid, or *maleïc acid dibromide,* forms large, well-shaped crystals, is easily soluble in cold water, melts at 160°, and with boiling water or heated alone to 180° splits up into hydric bromide and the so-called isobrom-maleïc acid.

Tartaric Acids, $C_4H_6O_6 = C_2H_2\begin{cases}(OH)_2\\(CO.OH)_2\end{cases}$

901. Four isomeric acids of this formula are known, apparently having the same structural formula, since they are not only directly convertible one into another, but also, by heating with fuming hydric iodide, they yield the same acid, ordinary succinic:

$$C_2H_2(OH)_2(CO.OH)_2 + 4HI = C_2H_4(CO.OH)_2 + 2OH_2 + 2I_2.$$

Two of them, in solution, rotate the plane of a ray of polarised light, *ordinary tartaric acid* to the right, *lævotartaric antitartaric acid* to an equal extent to the left.

The other two are optically inactive.

Racemic acid is a combination of ordinary and lævotartaric, into both of which modifications it may be decomposed.

Inactive or *mesotartaric* is not decomposable into an active and inactive acid.

Metatartaric is a further modification, produced by fusion of ordinary tartaric; it is uncrystallisable.

Ordinary or Dextro-tartaric Acid

902. Is found in many fruits, particularly in the juice of ripe grapes, generally along with a smaller amount of lævotartaric acid, as acid potassic salt, which during the fermentation of the must, by reason of the formation of alcohol, is deposited, mixed with yeast, calcic tartrate colouring matters, &c., in crusts, constituting crude tartar or argol.

It is purified by recrystallisation from boiling water, with the addition of animal charcoal to remove the colouring matters, when it forms a white, finely crystalline powder (*cream of tartar*).

In the preparation of the free acid the crude tartar is first boiled with powdered chalk:

$$2C_4H_5KO_6 + CaCO_3 = CO_2 + OH_2 + C_4H_4CaO_6 + C_4H_4K_2O_6,$$

insoluble calcic tartrate and very soluble neutral potassic tartrate being formed, the latter of which is also precipitated as the insoluble calcic salt by the addition of calcic chloride solution. The united precipitates are well washed and decomposed by the requisite quantity of dilute sulphuric acid. The tartaric acid solution is separated from the calcic sulphate precipitate, and by evaporation and subsequent cooling deposits large anhydrous crystals of the free acid. If the raw material contains lævotartaric acid, this will combine during the crystallisation with an equal amount of dextro-acid to form racemic acid, the crystals of which, containing water of crystallisation, effloresce in a warm atmosphere, and may be easily distinguished by their clouded appearance from those of ordinary tartaric acid and mechanically separated.

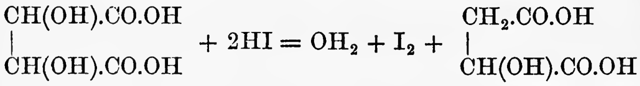
Dextro-tartaric acid forms large monoclinic prisms; very often half only of certain of the truncating faces are developed. They exhibit the property of pyro-electricity. On warming the right hemihedric faces become negative and on cooling positive.

Tartaric acid is very soluble in water (in about half its weight by ordinary temperatures), difficultly in alcohol, and not at all in ether. Its solutions rotate the plane of a ray of polarised light to the *right* ($\alpha = +9{\cdot}6^\circ$ at 21°).

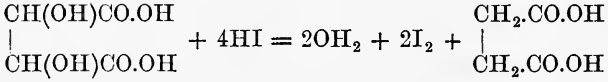
By heating to 170° tartaric acid melts, and passes without alteration of composition into an amorphous modification, the so-called *metatartaric acid.* It crystallises from its solutions after a very long time. At a little higher temperature it boils up, giving off water, and is converted into bodies corresponding to the ethereal anhydrides of the lactic series of acids, which are not yet sufficiently investigated to be described in detail. Long-continued heating to 180° finally converts the acid into a white powder, insoluble in water, of the atomic constitution $C_4H_4O_5$, and commonly called *tartaric anhydride,* since by boiling with water or alkalies it yields the acid or its salts; at the same time it is doubtless merely an ethereal anhydride.

At a still higher temperature the smell of burnt sugar makes itself apparent, dry distillation commencing with formation of carbonic acid, water, acetic acid, pyrotartaric (§ 838, 2) and pyroracemic acids (§ 803).

Heated with fuming HI to 120°, tartaric acid is reduced first to malic and finally to succinic acid:



$$\begin{array}{l}CH(OH).CO.OH\\ |\\ CH(OH).CO.OH\end{array} + 2HI = OH_2 + I_2 + \begin{array}{l}CH_2.CO.OH\\ |\\ CH(OH).CO.OH\end{array}$$



$$\begin{array}{l}CH(OH)CO.OH\\ |\\ CH(OH)CO.OH\end{array} + 4HI = 2OH_2 + 2I_2 + \begin{array}{l}CH_2.CO.OH\\ |\\ CH_2.CO.OH\end{array}$$

The acid is easily altered by oxidising agents, especially when heated.

With manganic oxide or potassic bichromate and sulphuric acid the acid yields in great part CO_2 and formic acid. Nitric acid gives principally oxalic acid, and on fusion with alkalies it gives acetic and oxalic acids; it reduces ammoniacal silver solutions, as well as auric and platinic chlorides, in the presence of alkalies to metal.

903. The *tartrates* known have been well investigated, and are especially characterised by their distinct crystallisation.

Three classes of salts are known, e.g. acid, neutral, and basic, in the latter of which the hydrogen of the alcoholic hydroxyl is displaced by a metal.

The neutral alkaline salts, such as

$$C_2H_2(OH)_2(CO.OK)_2,\ C_4H_4Na_2O_6,OH_2,\ C_4H_4(NH_4)_2O_6,$$

are easily soluble in water.

The acid salts are more difficultly soluble, the potassium and ammonium salts more so than the sodium salt, $C_4H_5NaO_6$. The *hydric potassic salt,* $C_4H_5KO_6$ (*cream of tartar*), requires 240 parts of cold and 14 parts of boiling water for solution.

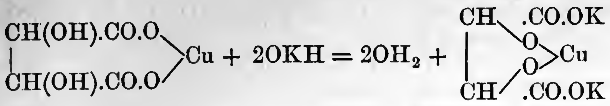
On exactly saturating a solution of cream of tartar with sodic carbonate and evaporating, *potassic sodic tartrate* (*Rochelle salt*) crystallises in very beautiful rhombic crystals with hemihedric faces, which are permanent in the air and have the composition:

$$C_4H_4KNaO_6 + 4OH_2.$$

The ammonium sodium salt is isomorphous with the latter.

The neutral *calcic salt,* $C_4H_4CaO_6 + 4OH_2$, exists in many plants, e.g. the vine, and hence occurs in crude tartar and wine yeast. It is a crystalline precipitate soluble in acids, including acetic, alkalies, and ammonic salts.

The *cupric salt* is also obtained by double decomposition as a crystalline precipitate, which dissolves in an alkaline solution to a deep blue liquid (*Fehling's* solution), a basic alkali copper salt being formed:

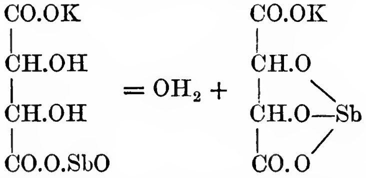


The same result is obtained by dissolving cupric hydrate in neutral alkaline tartrates, or by mixing copper salts with tartaric acid and an excess of alkalies. The copper cannot be precipitated from this solution by means of caustic alkalies. Tartaric acid acts in a similar manner towards aluminium, iron, zinc, tin, and other metals in solution in presence of excess of alkali.

Plumbic tartrate, $C_4H_4PbO_6$, is a white voluminous precipitate soluble in ammonia water, which on boiling deposits half of the tartaric acid as basic plumbic salt:

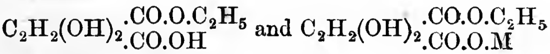
$$C_4H_2Pb_2O_6 = C_2H_2(O_2Pb):(CO.O)_2Pb.$$

Antimonic oxide dissolves in a boiling solution of cream of tartar to *antimonyl potassic tartrate* (*tartar emetic*), which, on cooling the concentrated *liquid*, crystallises in colourless shining octahedra or tetrahedra of the formula $2(C_4H_4KSbO_5) + OH_2$. They lose their water of crystallisation at 100°, and at 200° pass by further loss of water into basic potassic antimon-tartrate:



Analogous compounds are formed with arsenious oxide and boric anhydride. Boryl potassic tartrate, $C_4H_4K(BO)O_6$, is amorphous and exceedingly soluble in water.

904. *Ethereal Salts and Amides of Tartaric Acid.*—By heating tartaric acid with alcohols acid salts are formed, and on evaporation crystallise; they are still capable of taking up an equivalent of a metal:



$$C_2H_2(OH)_2\begin{matrix}.CO.O.C_2H_5\\.CO.OH\end{matrix} \text{ and } C_2H_2(OH)_2\begin{matrix}.CO.O.C_2H_5\\.CO.O.M\end{matrix}$$

Monethylic tartrate.

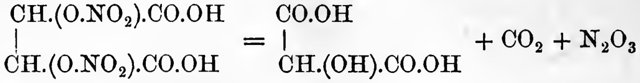
The normal ethereal salts are formed, like those of malic acid (§ 861), by saturating an alcoholic tartaric acid solution with HCl, neutralising the product with sodic carbonate, and shaking out with ether.

Diethylic tartrate, $C_2H_2(OH)_2:(CO.O.C_2H_5)_2$, is a neutral liquid, decomposing on distillation; on mixing with water it is quickly decomposed into alcohol, monethylic tartrate, and free acid. On gently warming the salt with alcoholic ammonia *tartramid*,

$C_2H_2(OH)_2(CO.NH_2)_2$, is obtained. It forms rhombic crystals soluble in water and alcohol.

905. Tartaric acid, as a dihydric alcohol, may have its hydroxyl groups replaced by acid radicals.

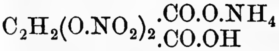
Dinitro-tartaric acid, $C_2H_2(O.NO_2)_2(CO.OH)_2$, can be obtained as a colourless mass of fine silky needles by treating tartaric acid with the strongest nitric acid with addition of sulphuric acid. The acid is particularly unstable, and decomposes in aqueous solutions at ordinary temperatures, and much more quickly at 30° into CO_2, N_2O_3, and tartronic acid (§ 859):



$$\begin{array}{l} CH.(O.NO_2).CO.OH \\ | \\ CH.(O.NO_2).CO.OH \end{array} = \begin{array}{l} CO.OH \\ | \\ CH.(OH).CO.OH \end{array} + CO_2 + N_2O_3$$

Oxalic acid is also always formed in some quantity, especially when warmed to 30°.

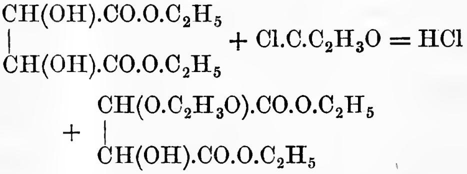
The acid ammonic salt of dinitro-tartaric acid:



$$C_2H_2(O.NO_2)_2\begin{array}{l}.CO.O.NH_4 \\ .CO.OH\end{array}$$

is difficultly soluble, the normal salt easily soluble in water; ammonic sulphide converts them both into tartaric acid, sulphur being precipitated.

Aceto-tartaric acids are formed when chlor-acetyl acts on tartaric acid. The ethereal salts are most easily obtained from the ether of tartaric acid:



$$\begin{array}{l} CH(OH).CO.O.C_2H_5 \\ | \\ CH(OH).CO.O.C_2H_5 \end{array} + Cl.C.C_2H_3O = HCl$$

$$+ \begin{array}{l} CH(O.C_2H_3O).CO.O.C_2H_5 \\ | \\ CH(OH).CO.O.C_2H_5 \end{array}$$

and $$C_2H_2(OH_2).(CO.O.C_2H_5)_2 + 2ClC_2H_3O = 2HCl + C_2H_2(O.C_2H_3O)_2(CO.OC_2H_5)_2.$$

Ethylic mono-aceto-tartrate is an oil which cannot be distilled unchanged; the *ethylic diaceto-tartrate*, however, forms prismatic crystals, fusing at 67° and distilling quite unchanged at 290°. It is easily soluble in alcohol and somewhat in warm water. Alkalies saponify it to alcohol and salts of acetic and tartaric acids.

Antitartaric Acid, $C_4H_6O_6$.

906. By saturating a hot solution of sodic racemate with ammonia the double salt $C_4H_4Na(NH_4)O_6 + 4OH_2$ is formed in large rhombic crystals, of which one half is identical in form with the right-handed sod-ammonic tartrate, possessing the hemipyramidal faces at the top whilst the faces of the other half are their images as seen in a mirror—that is, they are the left-sided hemihedra of the pyramid. The solutions of the latter salt turn the ray of polarised light to the left. The crystals are of the same form as tartaric acid, but the hemidhedral faces are on the left side. They are pyro-electric, on warming negative, on cooling positive. Its solutions rotate ($\alpha = -9{\cdot}6°$ at 21° C.) to the left. It exhibits otherwise all the properties of ordinary tartaric acid.

Racemic Acid, $C_8H_{12}O_{12},2OH_2 = rC_4H_6O_6,lC_4H_6O_6,2OH_2$.

907. By mixing cold saturated solution of equal quantities of the two optical modifications of tartaric acid heat is evolved, and an optically inactive acid is produced, crystallising in oblique prisms. The acid is also sometimes found in crude tartaric acids. Ordinary tartaric acid may be heated to 100° without any apparent change, but the crystals of racemic acid lose water and become cloudy, and may then be mechanically separated. Racemic acid requires 5·7 times its weight of water at 15° for solution.

Mesotartaric Acid, $C_4H_6O_6$.

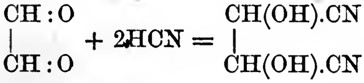
908. The three modifications of acid described yield, when heated with water to about 160°, an optically inactive modification, which cannot again be separated into two modifications. Its potassium and calcium salts are also much more soluble. Its crystals resemble those of tartaric acid and melt at 140°.

909. *Conversion of Tartaric Acid into its Modifications.*—If any of the optically active varieties of tartaric acid be heated with a tenth of its weight of water to 175° for some time, it passes to some extent into racemic acid, or rather a portion is changed into the opposite kind, which combines with the unchanged acid to form racemic acid. A small quantity of inactive acid is also simultaneously produced. If the temperature be allowed to rise to 165° only, much of this inactive variety is produced. It may be converted for the greater part into racemic acid on raising the temperature to about 175°.

910. *Synthetical Production of Tartaric Acid.*—Tartaric acid is obtained by boiling the argentic salt of dibrom succinic acid with water:

$$C_2H_2Br_2(CO.OAg)_2 + 2OH_2 = 2AgBr + C_2H_2(OH)_2(CO.OH)_2.$$

Racemic acid is generally found in the first crystallisation, some inactive acid remaining in the liquid. Different modifications are also found in the acid synthesised from glyoxal and hydrocyanic acid (§ 754) and subsequent boiling of the cyanide with hydric chloride:



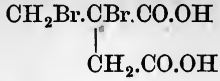
$$\begin{array}{l}CH:O\\ |\\ CH:O\end{array} + 2HCN = \begin{array}{l}CH(OH).CN\\ |\\ CH(OH).CN\end{array}$$

Mannite, dulcite, sugars, and various other carbohydrates yield tartaric acids on oxidation.

Compounds of Homologues of the Tartaric Acid Radical.

911. The pyrocitric acids combine with halogens, similarly to maleïc and fumaric acids, to form dibrom tartaric acids. Itaconic acid gives

Itadibrom-pyrotartaric acid, $C_5H_6Br_2O_4$:



$$\begin{array}{l}CH_2Br.CBr.CO.OH\\ \qquad\quad\;|\\ \qquad\quad CH_2.CO.OH\end{array}$$

which forms colourless, easily soluble crystals. Its salts decompose very easily, its silver salt giving, on boiling with water, *homotartaric acid*, $C_3H_4(OH)_2(CO.OH)_2$, which is difficult to crystallise.

The sodium salt decomposes on boiling with water into aconic acid and sodic bromide :

$$C_5H_4Na_2Br_2O_4 = 2NaBr + C_5H_4O_4.$$

Citra-dibrom-pyrotartaric acid, isomeric with the above, is a very soluble acid. Its salts decompose on boiling with water into metallic bromide and salts of *brom-meth-acrylic acid*, $C_4H_4BrNaO_2$.

Mesa-dibrom-pyrotartaric acid, from mesaconic acid, resembles the above acids in its chemical behaviour, and its salts also decompose into brom-meth-acrylic acid (§ 796) on boiling.

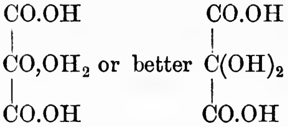
Dibrom-adipic acid, $C_6H_8Br_2O_4$, is an addition product of hydromuconic acid. It forms small difficultly soluble needles, melting with decomposition at 190°.

DIBASIC KETONIC ACIDS.

Mesoxalic Acid, $C_3H_2O_5,OH_2$

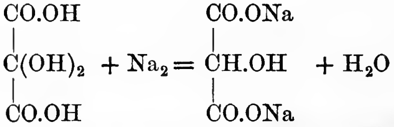
912. Mesoxalic acid is obtained from its derivatives in the urea group, alloxan and alloxanic acid, by the action of basic hydrates. On boiling a solution of baric alloxanate, baric mesoxalate deposits in small plates. The free acid crystallises with one molecule of water in deliquescent prisms, which melt at 115° without giving up any water.

Its constitutional formulæ may be represented by



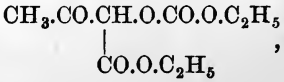
$$\begin{array}{l}CO.OH\\ |\\ CO,OH_2\\ |\\ CO.OH\end{array}\text{ or better }\begin{array}{l}CO.OH\\ |\\ C(OH)_2\\ |\\ CO.OH\end{array}$$

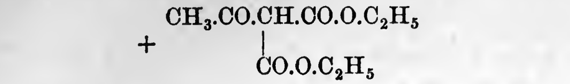
Sodium amalgam reduces it to tartronic acid (§ 859):



$$\begin{array}{l}CO.OH\\ |\\ C(OH)_2\\ |\\ CO.OH\end{array} + Na_2 = \begin{array}{l}CO.ONa\\ |\\ CH.OH\\ |\\ CO.ONa\end{array} + H_2O$$

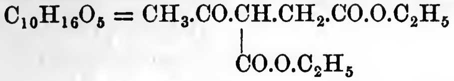
913. Several acids belonging to this group have been synthesised by the action of haloid substituted fatty acids on ethylic sod-aceto-acetate (§ 784).

Ethylic aceto-malonate,  $\begin{array}{l}CH_3.CO.CH.O.CO.O.C_2H_5\\ \qquad\quad\;|\\ \qquad\quad CO.O.C_2H_5\end{array}$, is a colourless, mobile liquid boiling at 237°–240°. It is obtained by the action of ethylic chloro-carbonate on ethylic sod-aceto-acetate:



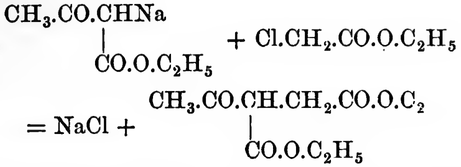
$$\begin{array}{l} CH_3.CO.CHNa.CO.O.C_2H_5 + Cl.CO.O.C_2H_5 = NaCl \\ \quad + \begin{array}{l} CH_3.CO.CH.CO.O.C_2H_5 \\ \qquad\quad | \\ \qquad\quad CO.O.C_2H_5 \end{array} \end{array}$$

Ethylic succin-aceto-acetate:



$$C_{10}H_{16}O_5 = \begin{array}{l} CH_3.CO.CH.CH_2.CO.O.C_2H_5 \\ \qquad\quad | \\ \qquad\quad CO.O.C_2H_5 \end{array}$$

is obtained by the action of ethylic monochlor acetate on ethylic sod-aceto-acetate:

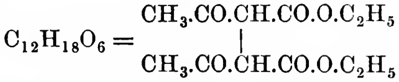


$$\begin{array}{l} \begin{array}{l} CH_3.CO.CHNa \\ \qquad\quad | \\ \qquad\quad CO.O.C_2H_5 \end{array} + Cl.CH_2.CO.O.C_2H_5 \\ = NaCl + \begin{array}{l} CH_3.CO.CH.CH_2.CO.O.C_2 \\ \qquad\quad | \\ \qquad\quad CO.O.C_2H_5 \end{array} \end{array}$$

It is a colourless ethereal liquid, boiling at 254°–256°, sp. gr. = 1·079 at 21°, insoluble in water, and gives no coloration with ferric chloride.

On saponification with baric hydrate it yields the baric salt of β-aceto-propionic acid, $CH_3.CO.CH_2.CH_2.CO.OH$ (§ 788, *b*).

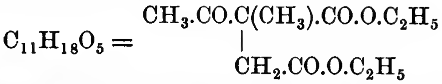
913*a*. *Ethylic diaceto succinate:*



$$C_{12}H_{18}O_6 = \begin{array}{l} CH_3.CO.CH.CO.O.C_2H_5 \\ \qquad\quad | \\ CH_3.CO.CH.CO.O.C_2H_5 \end{array}$$

is formed by the exact decomposition of ethylic sod-aceto-acetate with iodine in colourless transparent rhombic plates, melting at 77° with partial decomposition.

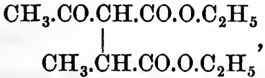
Ethylic a-methyl aceto-succinate:



$$C_{11}H_{18}O_5 = \begin{array}{l} CH_3.CO.C(CH_3).CO.O.C_2H_5 \\ \qquad\quad | \\ \qquad\quad CH_2.CO.O.C_2H_5 \end{array}$$

obtained from the action of methylic iodide, is a colourless oil, boiling at 263°.

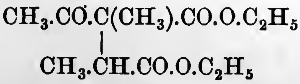
The β-compound,



$$\begin{array}{l} CH_3.CO.CH.CO.O.C_2H_5 \\ \qquad\quad | \\ CH_3.CH.CO.O.C_2H_5 \end{array}$$

, prepared from ethylic a-brom propionate and ethylic sod-aceto-acetate, boils at 257°–259°. Both acids are split up by alkalies into methyl succinic acid.

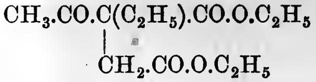
Ethylic a-β-dimethyl aceto-succinate:



$$\begin{array}{l} CH_3.CO.C(CH_3).CO.O.C_2H_5 \\ \qquad\quad | \\ CH_3.CH.CO.O.C_2H_5 \end{array}$$

is a colourless oil boiling at 270°–272°.

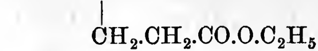
Ethylic α-ethyl aceto-succinate:



$$\begin{array}{l} CH_3.CO.C(C_2H_5).CO.O.C_2H_5 \\ \qquad\qquad | \\ \qquad\qquad CH_2.CO.O.C_2H_5 \end{array}$$

boils at 263°–265°. It is not acted upon by sodium.

An isomeric β-compound of nearly the same boiling point is acted upon by sodium with great violence.



Ethylic aceto-glutarate, $\begin{array}{l} CH_3.CO.CH.CO.O.C_2H_5 \\ \qquad\quad | \\ \qquad\quad CH_2.CH_2.CO.O.C_2H_5 \end{array}$, is a liquid of boiling point 271°–272°, resulting from the action of ethylic β-iodo-propionate on ethylic sod-aceto-acetate. It gives glutaric acid on saponification.

Ethylic aceto-tricarballylate:

$$CH_3.CO.C(CH_2.CO.O.C_2H_5)_2.CO.O.C_2H_5,$$

from the action of ethylic monochlor acetate on ethylic sod-aceto-succinate, is a thick yellow oil, giving tricarballylic acid on saponification.

URIC ACID, ITS DERIVATIVES AND RELATED BODIES.

914. Probably uric acid may be considered as a derivative of the tricarbon octavalent nucleus; in any case it stands in very close relationship to mesoxalic acid. Its composition is $C_5H_4N_4O_3$, but in what manner the elements are united to one another is not yet known with certainty, and the numerous constitutional formulæ proposed for it require a better foundation.

The expression given here can therefore have little but hypothetical value; nevertheless it corresponds best with the numerous known metamorphoses of uric acid.

Uric Acid, $C_5H_4N_4O_3$.

915. Uric acid is a general constituent of the urine of the vertebratæ, and is therefore an important product of the retrogressive metamorphosis of the nitrogenous constituents of animal tissue. It occurs in only small quantity in human and mammalian urine, least of all in that of herbivoræ, whilst its acid ammonic salt forms the chief constituent of the solid urine mass of birds, amphibia, and many insects. Human urine contains under normal circumstances so little urates that they remain completely dissolved after cooling, and only precipitate some crystalline uric acid after acidulation with hydrochloric acid. On greater secretion by the kidneys urine often deposits sediments of urates, or if increased still more they form concretions in the bladder (gravel or calculi).

Uric acid is generally prepared from serpents' excrements or from guano. The first is boiled with dilute solution of potassic or sodic hydrate; the hot filtered solution then contains the dibasic salt, e.g. $C_5H_2K_2N_4O_3$. On passing carbonic anhydride one half the metal is removed and the difficultly soluble monobasic salt precipitated:

$$2C_5H_2K_2N_4O_3 + CO_2 + H_2O = K_2CO_3 + 2C_5H_3KN_4O_3,$$

and this after washing decomposed by hydrochloric acid.

To prepare it from guano, the latter is boiled with a solution of one part of borax in 20 parts of water; the solution, on acidulating, gives a brown impure precipitate of uric acid, which is then purified as in the former method.

Uric acid forms a snow-white, spongy, micro-crystalline powder, destitute of smell and taste, but reacting on vegetable colours like a weak acid. It requires 1,800 parts of boiling and 14,000 parts of cold water for solution. It is insoluble in alcohol and ether.

On heating with concentrated sulphuric acid it dissolves, and on cooling yields deliquescent crystals of $C_5H_4N_4O_3,2H_2SO_4$, decomposed by water into their components. It gives two series of salts with the metals of the alkalies and alkaline earths, according as to whether one or two hydrogen atoms are replaced. The first, monobasic *urates*, are formed by the action of uric acid on carbonates, the dibasic only by means of basic hydrates. The latter yield one-half of their metal to carbonic anhydride.

Dipotassic urate, $C_5H_2K_2N_4O_3$, crystallises in fine needles, soluble in 44 parts of cold water and of strongly alkaline reaction.

Potassic urate, $C_5H_3KN_4O_3$, requires 800 parts of water for solution and is of neutral reaction. The sodic salts behave similarly.

Ammonic urate, $C_5H_3(NH_4)N_4O_3$, is formed by adding aqueous ammonia to uric acid, and frequently occurs in urine. It requires 1,600 parts of cold water for solution. *Calcic diurate*, $(C_5H_3N_4O_3)_2Ca$, is the most soluble of the alkaline earth salts, dissolving in 600 parts of water.

If uric acid be evaporated with strong nitric acid on the water bath, a yellowish residue is left, which is coloured purple-red by ammonia (murexide reaction).

On dry distillation uric acid yields much ammonic carbonate and hydrocyanic acid, together with ammonic cyanide, urea, cyanuric acid, &c., and leaves nitrogenous charcoal. By heating at 160° with concentrated hydriodic acid it is decomposed into carbonic anhydride, ammonic iodide, and glycocine:

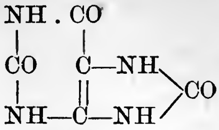
$$C_5H_4N_4O_3 + 5H_2O + 3HI = 3CO_2 + 3NH_4I + C_2H_5NO_2.$$

916. On oxidation uric acid yields various products, according as it occurs in acid or alkaline solution, and whether the oxidation is moderate or energetic. These oxidation products all appear by their further reactions to be urea derivatives of acid radicals; urea and its decomposition products are mostly formed at the same time.

The oxidation products may be placed under the following heads:—

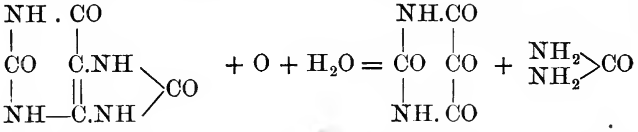
1. In acid solution.
    a. By moderate oxidation, urea and alloxan (mesoxalyl urea).
    b. By vigorous oxidation, parabanic acid (oxalyl urea).
2. In alkaline solution by absorption of atmospheric oxygen there are formed uroxonic acid, $C_5H_8N_4O_6$, together with oxonic acid, which readily decomposes into glyoxalyl urea, carbonic anhydride, and ammonia.
3. By plumbic dioxide potassic ferricyanide or potassic permanganate allantoïn is formed, which readily decomposes into urea and hydantoïn (glycolyl urea).

It is therefore very probable that uric acid contains a tricarbon nucleus and two urea nuclei, $CO.(NH)_2$, and it may therefore be expressed by the formula:

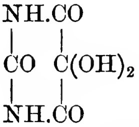


There is some reason to believe that the collection of CO groups round the imid residue would cause the hydrogen of the latter to be replaceable by metals (comp. § 826).

917. *Alloxan*, $C_4H_2N_2O_4$, or $CO\genfrac{}{}{0pt}{}{.NH.CO}{.NH.CO}CO$, mesoxalyl urea, is formed, together with urea, by adding uric acid in small portions to cooled nitric acid of sp. gr. 1·4 as long as the evolution of ruddy fumes continues. The alloxan, which then separates as a white crystalline powder, is collected on an asbestos filter and crystallised from warm water. Much alloxan is also formed by the carefully conducted action of hydrochloric acid and potassic chlorate on uric acid. The change may be expressed by the equation:

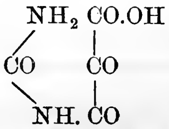


From a lukewarm saturated solution alloxan crystallises in large colourless rhombic prisms of the formula $C_4H_2N_2O_4,4H_2O$, which effloresce in dry air with loss of three molecules of water. The compound $C_4H_2N_2O_4,H_2O$ is obtained by evaporation of a hot solution in small monoclinic crystals, which lose the last molecule of water at 150° and then turn brown. Therefore the constitutional formula of alloxan is more probably:



(comp. mesoxalic acid, § 912). A solution of alloxan imparts a red colour and unpleasant odour to the skin. It gives a deep indigo blue colour with ferric chloride, and as a ketone body gives beautiful crystalline compounds with alkaline sulphites.

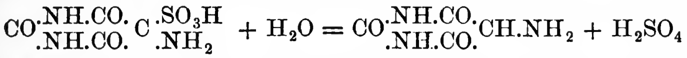
By baryta water or dilute potassic hydrate it is converted into salts of

Alloxanic acid, $C_4H_4N_2O_5 =$  . This is usually effected by mixing saturated solutions of alloxan and baric chloride, gently warming, and adding potassic hydrato until a permanent precipitate is produced. After short standing *baric alloxanate*,

$C_4H_2BaN_2O_5,4H_2O$, separates in small scaly crystals, which are difficultly soluble; on addition of the requisite quantity of sulphuric acid, free alloxanic acid is obtained, and on evaporation below 40° forms a syrup, solidifying after a time in fibrous crystals. Alloxanic acid is very soluble in water, reacts strongly acid, and forms true salts with one equivalent of metal, e.g. $NH_2.CO.NH.CO.CO.CO.OK$, in which, by addition of strong bases, another hydrogen atom can be replaced, $NH_2.CO.NK.CO.CO.CO.OK$(?). On boiling the latter compounds with water urea and a mesoxalate are formed:

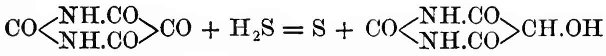
$$NH_2CO.NK.CO.CO.CO.OK + H_2O = NH_2.CO.NH_2 \\ + KO.CO.CO.CO.OK.$$

918. *Thionuric acid*, $C_4H_5N_3SO_6$. On mixing a solution of uric acid with sulphurous acid, and then with ammonic carbonate, there is formed on long boiling *ammonic thionurate*, which separates on cooling in nacreous four-sided scales, $C_4H_3(NH_4)_2N_3SO_6,H_2O$. Its solution gives a white precipitate with plumbic acetate of *plumbic thionurate*, from which, by dry decomposition with sulphuretted hydrogen, *thionuric acid* is obtained in solution. By evaporation the acid is obtained in very acid needles, yielding uramile and free sulphuric acid when boiled with water:



$$CO\begin{matrix}.NH.CO.\\.NH.CO.\end{matrix}C\begin{matrix}.SO_3H\\.NH_2\end{matrix} + H_2O = CO\begin{matrix}.NH.CO.\\.NH.CO.\end{matrix}CH.NH_2 + H_2SO_4$$

919. *Dialuric acid, tartronyl urea*, $C_4H_4N_2O_4$, is formed by addition of hydrogen to alloxan, when a boiling solution of the latter is treated with sulphuretted hydrogen till no more sulphur is precipitated:



$$CO<\begin{matrix}NH.CO\\NH.CO\end{matrix}>CO + H_2S = S + CO<\begin{matrix}NH.CO\\NH.CO\end{matrix}>CH.OH$$

From the filtered solution it is precipitated as an ammonic derivative on addition of ammonic carbonate, and after washing is dissolved in warm hydrochloric acid; on cooling dialuric acid crystallises out.

Addition of hydrogen also occurs on heating a solution of alloxan with hydrochloric acid and stannous chloride. On mixing together alloxan and an alkaline carbonate, and adding some hydrocyanic acid, carbonic anhydride is evolved, potassic dialurate separates, whilst potassic oxalurate remains dissolved:

$$2C_4H_2N_2O_4 + K_2CO_3 + H_2O = C_4H_3KN_2O_4 \\ + C_3H_3KN_2O_4 + 2CO_2.$$

Dialuric acid crystallises in long needles, which are pretty soluble, react strongly acid, and absorb oxygen from the air with conversion into alloxantin.

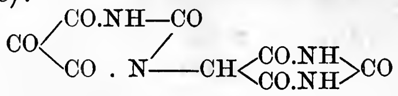
920. *Alloxantin*, $C_8H_4N_4O_7,3H_2O$, separates when solutions of equal molecules of alloxan and dialuric acid are mixed:

$$C_4H_2N_2O_4 + C_4H_4N_2O_4 = H_2O + C_8H_4N_4O_7.$$

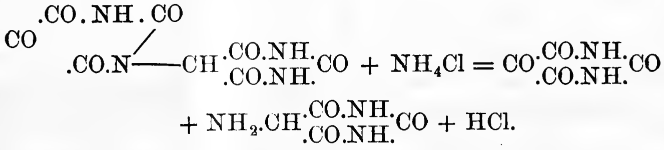
In consequence of this it is formed by passing sulphuretted hydrogen into a cold solution of alloxan, and then precipitates with sulphur; it is also formed by dropping stannous chloride mixed with strong hydrochloric acid into an aqueous solution of alloxan and by the moderated oxidation of dialuric acid.

Alloxantin crystallises in small hard prisms difficultly soluble in cold water. It gives a beautiful blue solution with ferric chloride and ammonia, a violet blue precipitate with baric hydrate, which on heating is decomposed into baric alloxanate and dialurate. At ordinary temperatures nitric acid oxidises it to alloxan.

The structural formula of alloxantin is analogous to that of oxalantin (§ 828):



921. *Uramil*, dialuramide or amido-malonyl urea, $C_4H_5N_3O_3$, is formed, as already mentioned (§ 918), from thionuric acid, and, together with alloxan, by mixing solutions free from air of alloxantin and ammonic chloride:



It crystallises in small white needles, insoluble in cold water. Nitric acid converts it into alloxan. It turns red on exposure to air.

On boiling uramil solution with potassic cyanate the potassic salt of pseudo-uric acid is obtained:

$$C_4H_5N_3O_3 + CO.NK = C_5H_5N_4KO_4,$$

which on addition of hydrochloric acid yields a powder consisting of small prisms of *pseudo-uric acid:*

$$CO\genfrac{}{}{0pt}{}{.NH.CO.}{.NH.CO.}CH.NH.CO.NH_2$$

922. *Murexide*, $C_8H_8N_6O_6,H_2O$, is the ammonic derivative of *purpuric acid*, which latter is not known in the free state. Murexide is formed when four parts of uramil are heated to boiling with three parts of mercuric oxide and water, and the deep red liquid filtered hot:

$$2C_4H_5N_3O_3 + HgO = Hg + C_8H_8N_6O_6 + H_2O.$$

On cooling murexide separates in difficultly soluble prisms or plates, having a metallic green lustre; they are deep red by transmitted light and yield a brown powder.

It is also formed by long exposure of dry alloxantin at 100° to an atmosphere of ammonia:

$$C_8H_4N_4O_7 + 2NH_3 = C_8H_8N_6O_6 + H_2O,$$

and by mixing ammoniacal solutions of uramil and alloxan:

$$C_4H_5N_3O_3 + C_4H_2N_2O_4 + NH_3 = C_8H_8N_6O_6 + H_2O.$$

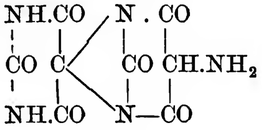
Purpurates of metals can be obtained by double decomposition between murexide and metallic salts; thus on boiling with potassic nitrate potassic purpurate is formed:

$$C_8H_4(NH_4)N_5O_6 + KNO_3 = C_8H_4KN_5O_6 + NH_4.NO_3,$$

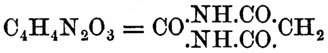
which on cooling gives crystals resembling those of murexide. Baric chloride precipitates a nearly black crystalline powder of baric purpurate, $(C_8H_4N_5O_6)_2Ba$.

Addition of acids to any of these compounds does not liberate purpuric acid, but gives uramil and alloxan.

Several probable constitutional formulæ can be written for purpuric acid in accordance with its method of formation and decomposition; these all come to the fact that the nitrogen bonds of one ingredient molecule must be saturated by the carbon bonds of the other, probably something like this:



923. *Barbituric acid,* malonyl urea:

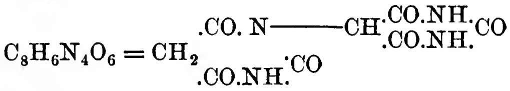


$$C_4H_4N_2O_3 = CO\begin{smallmatrix}.NH.CO.\\ .NH.CO.\end{smallmatrix}CH_2$$

is formed by heating alloxantin with two to three times its weight of concentrated sulphuric acid on the water bath until the evolution of sulphurous anhydride ceases. As soon as cold the thick liquid is diluted with an equal volume of water, when a difficultly soluble compound separates, which on recrystallisation from hot water gives crystalline barbituric acid whilst parabanic acid remains in solution.

Barbituric acid crystallises in large colourless rhombic prisms difficultly soluble in cold water; it exchanges one or two hydrogen atoms for metal when treated with strong bases, and on boiling with dilute alkalies yields a malonate and urea, or its decomposition products ammonia and a carbonate.

Hydurilic acid:



$$C_8H_6N_4O_6 = CH_2\begin{smallmatrix}.CO.\,N\text{———}CH\begin{smallmatrix}.CO.NH.\\ .CO.NH.\end{smallmatrix}CO\\ \\ .CO.NH.\cdot CO\end{smallmatrix}$$

is formed as its difficultly soluble ammonium derivative, together with carbonic anhydride and formic acid, by heating dialuric acid in glycerin at 140°–160°, and, together with glycocine and pseudoxanthin, when uric acid is heated at 110°–130° with double its weight of strong sulphuric acid and the solution poured into much water. The free acid crystallises in the cold with two molecules of water in small prisms; from hot solutions, with one molecule of water, in rhombic tables. It is difficultly soluble in cold water and exchanges two atoms of hydrogen for metal. Both acid and salts give a dark green coloration with ferric chloride. Cold concentrated nitric acid oxidises it to alloxan, nitric acid of sp. gr. 1·2 to violuric acid, and acid of 1·35 sp. gr., especially on warming, converts it into dilituric acid and alloxan.

924. *Dilituric acid,* nitro-barbituric acid, or nitro-malonyl urea,

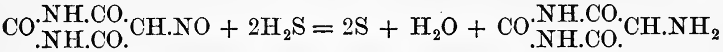
$C_4H_3(NO_2)N_2O_3,3H_2O$, is formed from barbituric acid by action of hot nitric acid. It crystallises in colourless prisms or leaves; these effloresce in dry air, dissolve readily in hot water, difficultly in cold with yellow coloration.

It has the properties of a very strong acid and can exchange all three hydrogen atoms for metal. The monobasic salts:

$$C_3H_2M(NO_2)N_2O_3,$$

are so stable that they are not decomposed by mineral acids.

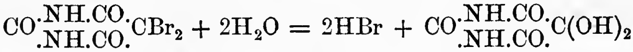
Violuric acid, nitroso-barbituric acid, or nitroso-malonyl urea, $C_4H_3(NO)N_2O_3$, is best prepared by heating hydurilic acid with potassic nitrite and acetic acid; potassic violurate crystallises out on cooling. This forms deep blue prisms or plates of the formula $C_4H_2K(NO)N_2O_3,2H_2O$, dissolving in water to a violet blue solution; it gives with baric chloride a reddish violet precipitate of baric violurate, from which the free acid can be liberated by addition of sulphuric acid. Violuric acid crystallises in yellow, rhombic prisms; they are pretty readily soluble, and are decomposed by excess of potassic hydrate into nitroso-malonic acid and urea, give dilituric acid on treatment with hot nitric acid, and are converted into uramil by reducing agents, such as hydric sulphide:



$$CO\begin{array}{l}.NH.CO.\\ .NH.CO.\end{array}CH.NO + 2H_2S = 2S + H_2O + CO\begin{array}{l}.NH.CO.\\ .NH.CO.\end{array}CH.NH_2$$

Brom-barbituric Acids.—By the action of bromine on barbituric, dilituric, or violuric acids there is first formed

Dibrom-barbituric acid, $C_4H_2Br_2N_2O_3$, which, forming plates readily soluble in water, alcohol, and ether, and on boiling with water, gives hydrobromic acid and alloxan:



$$CO\begin{array}{l}.NH.CO.\\ .NH.CO.\end{array}CBr_2 + 2H_2O = 2HBr + CO\begin{array}{l}.NH.CO.\\ .NH.CO.\end{array}C(OH)_2$$

Aqueous hydrocyanic acid converts it into cyanogen bromide and

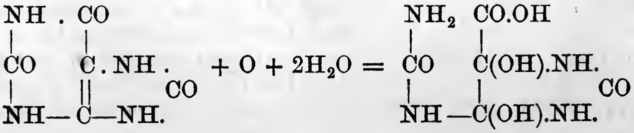
Monobrom-barbituric acid, $C_4H_3BrN_2O_3$, separating in aggregates of needles difficultly soluble in water.

Nascent hydrogen reconverts both brom-acids into barbituric acid.

925. *Uroxanic acid*, $C_5H_8N_4O_6$, is obtained by oxidation of uric acid in alkaline solution, when that is exposed for some months to the action of atmospheric oxygen, until uric acid is no longer precipitated on acidulation. On cooling to −5° potassic uroxanate:

$$C_5H_6K_2N_4O_6,3H_2O,$$

separates in nacreous plates, whilst potassic oxonate remains in solution. From the potassic salt hydrochloric acid separates moxanic acid in colourless prisms, decomposed with evolution of carbonic anhydride on boiling with water. Uroxanic acid is derived from uric acid by addition of two molecules OH_2 and one atom of oxygen, probably thus:



$$\begin{array}{llll} NH\ .\ CO & & & \\ | \quad\quad | & & & \\ CO \quad C.NH. & & & \\ | \quad\quad \| & CO & & \\ NH—C—NH. & & & \end{array} + O + 2H_2O = \begin{array}{lll} NH_2 & CO.OH & \\ | & | & \\ CO & C(OH).NH. & \\ | & | & CO \\ NH & —C(OH).NH. & \end{array}$$

The mother liquor from which potassic uroxanate has been separated yields on evaporation needles of dibasic *potassic oxonate:*

$$2C_4H_3K_2N_3O_4,3H_2O,$$

from whose cold saturated solution cautious addition of acetic acid separates the monobasic *potassic oxonate,* $C_4H_4KN_3O_4$, this also crystallising in needles; but further decomposition readily ensues, carbonic anhydride being evolved and a crystalline powder of *potassic lantanurate* separating:

$$C_4H_3K_2N_3O_4 + 2HO.C_2H_3O + H_2O = KO.C_2H_3O$$
$$+ (NH_4)O.C_2H_3O + C_3H_3KN_2O_3 + CO_2.$$

926. Hot concentrated nitric acid converts both uric acid and alloxan, with evolution of carbonic anhydride, into *parabanic acid,* $C_3H_2N_2O_3$, which as oxalyl urea (§ 826) has been already mentioned together with its derivatives *oxaluric acid, oxaluramide,* and oxalantin.

Allantoïn, $C_4H_6N_4O_3$, is formed in the oxidation of uric acid by plumbic peroxide, potassic ferricyanide, or potassic nitrite and acetic acid, and occurs naturally in the urine of young calves and in the allantoïc liquid of the cow. From these liquids it is obtained by evaporation and cooling, best from uric acid by boiling with water under slow addition of plumbic dioxide. The liquid filtered from some plumbic oxalate is treated with hydric sulphide to remove lead, and the clear solution evaporated to crystallisation, whereby allantoïn separates whilst some urea remains dissolved.

Allantoïn crystallises in colourless prisms, little soluble in cold water. Its hot aqueous solution, on addition of argentic nitrate and ammonia, gives a white crystalline precipitate of silver allantoïn, $C_4H_5AgN_4O_3$. By heating with hydriodic acid allantoïn is decomposed into urea and hydantoïn (glycolyl urea, § 724):

$$C_4H_6N_4O_3 + 2HI = I_2 + CON_2H_4 + C_3H_4N_2O_2.$$

The formation of allantoïn from uric acid is expressed by

$$C_5H_4N_4O_3 + H_2O + O = CO_2 + C_4H_6N_4O_3$$

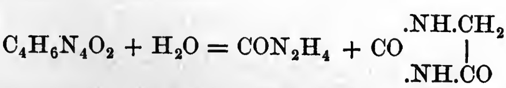
(comp. alloxan, § 917).

On dissolving allantoïn in solution of potassic hydrate, and after some time adding acetic acid and alcohol, crystals of potassic allantoate separate:

$$C_4H_6N_4O_3 + KOH = C_5H_7KN_4O_4.$$

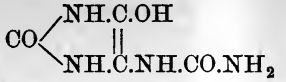
An aqueous solution of allantoïn, on treatment with sodium amalgam, unites with hydrogen, eliminating water and forming

Glycoluril, $C_4H_6N_4O_2$, forming colourless octahedra or needles, and decomposing on boiling with acids or alkalies into urea and hydantoïn:

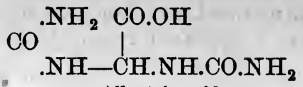


$$C_4H_6N_4O_2 + H_2O = CON_2H_4 + CO\begin{array}{l}.NH.CH_2\\ \quad\;|\\ .NH.CO\end{array}$$

These relations give the following plausible structural formulæ for allantoïn and its derivatives:



Allantoïn.



$$\mathrm{CO}\begin{array}{l}.\mathrm{NH_2}\ \ \mathrm{CO.OH}\\ \qquad\quad\ \ |\\ .\mathrm{NH{-}CH.NH.CO.NH_2}\end{array}$$

Allantoic acid.

$$\mathrm{CO}\begin{array}{l}.\mathrm{NH.CH}\\ \qquad\ \ \|\\ .\mathrm{NH.C.NH.CO.NH_2}\end{array}$$

Glycoluril.

Allantoïn dissolved in solution of potassic hydrate is oxidised by addition of four times its weight of potassic ferricyanide to *potassic allantoxanate*, $C_4H_2KN_3O_4$; this, on addition of acetic acid, separates in difficultly soluble silky needles:

$$C_4H_6N_4O_3 + KOH + O = C_4H_2KN_3O_4 + NH_3 + H_2O.$$

Bodies Related to Uric Acid.

Xanthine, $C_5H_4N_4O_2$.

927. Xanthine was first discovered as the chief constituent of a rare form of urinary calculi; later it was obtained from guanine, and afterwards recognised as a body widely disseminated in the animal organism, though occurring in but small quantity. It occurs constantly in minute quantity in human urine, the amount being increased by the continued use of sulphur baths. From uric acid, with which it differs in composition only by containing one atom less of oxygen, it can be obtained by reduction with sodium amalgam. That an isomeric body, *pseudoxanthine*, can be obtained together with hydurilic acid and glycocine by heating uric acid with strong sulphuric acid has already been mentioned.

It is obtained most abundantly from guanine. This is dissolved in hot strong nitric acid, and potassic nitrite added as long as large quantities of red vapours are evolved. On diluting with water, red flocks of a mixture of xanthine and pseudoxanthine are obtained; these are dissolved in boiling ammonia, and, in order to reduce the nitro-compound, treated with ferrous sulphate solution as long as black ferroso-ferric oxide separates. On evaporation the filtrate yields a mixture of xanthine and ammonic sulphate, from which the latter can be extracted by cold water.

Xanthine is a white amorphous powder scarcely soluble in cold, very difficultly in hot water. It is largely dissolved by strong acids, especially when hot, yielding crystalline salts with them, which, however, are decomposed by water.

Argentic nitrate gives with a nitric acid solution of xanthine a white precipitate, $C_5H_4N_4O_2,AgO.NO_2$, which can be crystallised in fine needles from hot nitric acid.

Xanthine is also soluble in the alkalies and in aqueous ammonia; from the latter solution argentic nitrate gives a gelatinous precipitate, $C_5H_2Ag_2N_4O_2,H_2O$.

Xanthine gives a yellow residue when evaporated with nitric acid, which gives with alkalies a reddish yellow coloration, becoming violet on evaporation.

928. *Guanine*, $C_5H_5N_5O = C_5H_4N_4O(NH)$, occurs in most guanos (about $\frac{3}{4}$ %), in the excrements of the garden spider, in the liver and pancreas gland, and in the scales of whiting. It also occurs in the flesh of hogs in the form of round white concretions during a disease of the animal.

To prepare it from guano, the latter is boiled with milk of lime, until a filtered sample appears colourless. The residue, consisting mainly of uric acid and guanine, is then boiled repeatedly with solution of sodic hydrate, and the filtered solution over-saturated with acetic acid. The precipitated mixture of uric acid and guanine is then extracted with nitric acid and the guanine precipitated with ammonia.

Guanine is a colourless amorphous powder insoluble in water and alcohol; it yields crystalline compounds with alkalies, acids, and some mineral salts. The metallic compounds contain two hydrogen atoms replaced by metal, e.g. $C_5H_3Na_2N_5O,2H_2O$, the salts either one or two equivalents of acid, e.g. $C_5H_5N_5O,2HCl$ and $C_5H_5N_5O,HCl$. The argentic nitrate compound, $C_5H_5N_5O,AgO.NO_2$, behaves analogously to the xanthine compound.

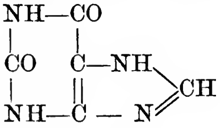
Nitrous acid converts guanine into xanthine, nitrogen being evolved:

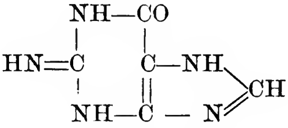
$$C_5H_4N_4O(NH) + HO.NO = N_2 + H_2O + C_5H_4N_4O_2.$$

Hydrochloric acid and potassic chlorate oxidise it to parabanic acid, guanidine, and carbonic anhydride:

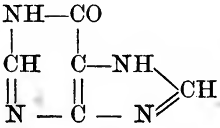
$$C_5H_4N_4O(NH) + H_2O + 3O = C_3H_2N_2O_3 + C(NH_2)_2NH + CO_2.$$

Therefore guanine and xanthine appear to be bodies of constitution analogous to uric acid, for which the following structural formula may be drawn (comp. § 916):





929. *Hypoxanthine*, or *sarcine*, $C_5H_4N_4O$, resembles xanthine and guanine in many points, and can be converted into the first on oxidation. It must therefore have an analogous constitutional formula, probably:



It is widely disseminated in the fluids of the animal body, occurring especially in muscle flesh of the vertebratæ, always accompanied by xanthine.

It can be obtained from extract of meat, after separation of the creatine (§ 728), by diluting the mother liquor and precipitating with cupric acetate at the boiling temperature. The smutty brown precipitate of copper hypoxanthine is dissolved in nitric acid, precipitated by argentic nitrate as *hypoxanthine argentic nitrate:*

$$C_5H_4N_4O,AgNO_3,$$

which is recrystallised from hot nitric acid. This is then boiled with ammoniacal silver solution to convert it into the insoluble *hypoxanthine silver*, $C_5H_2Ag_2N_4O,H_2O$, and this latter—suspended in water—decomposed by sulphuretted hydrogen. The precipitate of argentic sulphide is then extracted with much boiling water and the hot filtered liquid evaporated.

The preparation so obtained is still contaminated with xanthine, from which it can only be incompletely separated, the purification being effected by the greater solubility of its *hydrochloride* :

$$C_5H_4N_4O,HCl,H_2O$$

(which crystallises in nacreous plates), and the more difficult solubility of its argentic nitrate compound in nitric acid.

Hypoxanthine crystallises in colourless microscopic needles; it is considerably more soluble in water than xanthine, as also in aqueous acids and alkalies.

With the latter and with baric hydrate it yields soluble crystalline compounds, e.g. $C_5H_2N_4OBa,2H_2O$.

930. *Carnine*, $C_7H_8N_4O_3,H_2O$, also occurs in extract of meat, and is probably the source of hypoxanthine. Extract of meat diluted with six times its weight of water is first precipitated with baryta water, and the filtrate with acetate of lead.

From this last precipitate much boiling with water extracts the lead compound of carnine, which is then decomposed with sulphuretted hydrogen and the filtrate evaporated to a small volume. Concentrated solution of argentic nitrate is then added, which gives a white flocculent precipitate of *carnine argentic nitrate*, $2C_7H_7AgN_4O_3,AgNO_3$, and this converted into *carnine silver* by treatment with dilute ammonia. This latter is finally suspended in water, decomposed by sulphuretted hydrogen, the carnine obtained by evaporation and purified by recrystallisation and treatment with animal charcoal.

Carnine is a colourless powder difficultly soluble in cold water. With hydrochloric acid it yields the compound $C_7H_8N_4O_3,HCl$, which crystallises well. By heating with nitric acid it is converted into hypoxanthine nitrate, with bromine into hypoxanthine hydrobromide. The other decomposition products obtained at the same time have not yet been characterised.

Theobromine and Caffeïne.

931. These weak vegetable bases appear to be methylated derivatives of xanthine. The first occurs in the cacao bean (from *Theobroma Cacao*), the latter in coffee berries, in the fruit of *Paulinia sorbilis*, in the leaves of the Chinese tea shrub and in those of *Ilex paraguensis* (Paraguay tea). Tea contains up to 4 %, coffee at most 1 %.

Both are obtained from the respective sources by extraction with water, precipitation of the tannic acid by plumbic acetate, removal of lead from the filtrate by hydric sulphide, and evaporation of the filtrate to crystallisation. The separated mass is then recrystallised from alcohol.

Theobromine, dimethyl xanthine, $C_7H_8N_4O_2 = C_5H_2(CH_3)_2N_4O_2$, is a powder difficultly soluble in boiling water and still less in alcohol and ether. It is dissolved by acids, forming crystalline salts, decomposed by water. It can be sublimed by careful heating. A crystalline precipitate of *argento-theobromine*, $C_7H_7AgN_4O_2$, is obtained on long boiling with ammoniacal argentic nitrate; and this precipitate, on heating with methylic iodide, yields, according to the equation:

$$C_7H_7AgN_4O_2 + CH_3I = AgI + C_7H_7(CH_3)N_5O_2,$$

Caffeïne, trimethyl xanthine, or methyl theobromine:

$$C_8H_{10}N_4O_2 \text{ or } C_5H(CH_3)_3N_4O_2.$$

It crystallises with a molecule of water in fine silky needles, which lose their water of crystallisation at 100°, melt at 225°, and sublime unaltered. If caffeïne is dissolved in chlorine water and the red brown spots left on evaporation heated with aqueous ammonia, a beautiful red violet coloration is obtained.

By boiling with baryta water caffeïne is converted, with separation of baric carbonate, into a strong base, *caffeïdine:*

$$C_8H_{10}N_4O_2 + Ba(OH)_2 = BaCO_3 + C_7H_{12}N_4O.$$

This, on long boiling with excess of baryta, decomposes into methylamine, ammonia, methyl-glycocine, and formic acid.

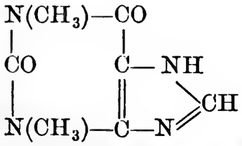
By aqueous chlorine or nitric acid caffeïne suffers a peculiar transformation into

Amalic acid, or tetramethyl alloxantine (comp. § 920):

$$C_{12}H_{14}N_4O_8 = C_8(CH_3)_4N_4O_7,H_2O,$$

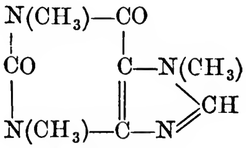
forming difficultly soluble crystals. With alkalies and baryta in the cold it gives a violet blue coloration, with ammonia in the air violet. It imparts a fine red colour to the skin. By further action of chlorine it yields *cholestrophane* (dimethyl parabanic acid, § 826). Theobromine behaves similarly towards chlorine.

The relations of theobromine and caffeïne to xanthine and uric acid are therefore unmistakable, and best find provisional expression in the formulæ:



Theobromine.

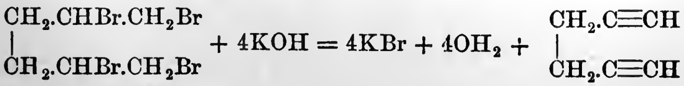
and



Caffeïne.

DIPROPARGYL, C_6H_6.

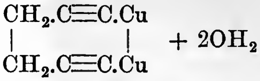
932. This hydrocarbon, isomeric with benzene, is obtained by long heating of diallyl tetrabromide with strong alcoholic potash, whereby an oil, boiling between 205°–210°, dibrom-diallyl, $C_6H_8Br_2$, is first formed, the final action being thus represented:



$$\begin{array}{l} CH_2.CHBr.CH_2Br \\ | \\ CH_2.CHBr.CH_2Br \end{array} + 4KOH = 4KBr + 4OH_2 + \begin{array}{l} CH_2.C{\equiv}CH \\ | \\ CH_2.C{\equiv}CH \end{array}$$

Dipropargyl (comp. § 804) is a colourless limpid liquid of 85° boiling point and sp. gr. ·81 at 18°.

It combines with copper and silver in ammoniacal solutions to compounds in which two hydrogen atoms are replaced by the metal :



$$\begin{array}{l} CH_2.C\equiv C.Cu \\ \vert \qquad\qquad\quad \vert \\ CH_2.C\equiv C.Cu \end{array} + 2OH_2$$

This body is yellow. The silver compound is at first white, but quickly blackens and decomposes. Hydrochloric acid regenerates the hydrocarbon.

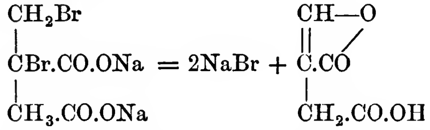
Bromine forms at first a thick liquid bromide, $C_6H_6Br_4$, which, when warmed with more bromine, gives a beautifully crystalline octobromide, $C_6H_6Br_8$, of melting point 140°.

DERIVATIVES OF THE HYDROCARBON NUCLEUS, C_nH_{2n-7}.

MONOBASIC ACIDS.

933. The monobasic acids known belonging to this group are aconic and muconic acids, which resemble paraconic and terebinic in their constitution (§§ 866, 867), only belong to a series containing two hydrogen atoms less.

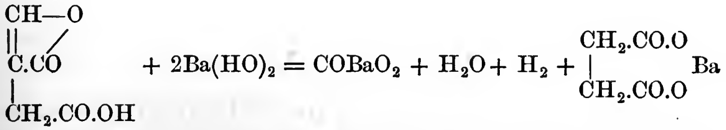
Aconic acid, $C_5H_4O_4$, results from boiling solutions of itadibrom pyrotartaric acid salts (§ 911):



better with addition of a molecule of sodic carbonate to two molecules of the salt. The sodium aconate, $C_5H_3NaO_4 + 3OH_2$, crystallises in fine leafy crystals.

Aconic acid forms large crystals with numerous faces, soluble in water, alcohol, and ether, and melting at 154°. With the exception of its silver salt, all its salts are easily soluble in water and crystallise exceedingly well.

By long boiling with $Ba(HO)_2$ aconic acid is decomposed into succinic and carbonic acids, and probably also a liquid acid richer in carbon:



Muconic acid, $C_6H_6O_4$, formed by the decomposition of dibromadipic acid (§ 911) by argentic oxide:

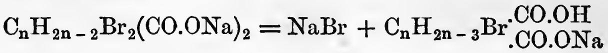
$$C_6H_8Br_2O_4 + Ag_2O = 2AgBr + OH_2 + C_6H_6O_4,$$

crystallises similarly to the aconic acid, dissolves easily in water, alcohol, and ether, and melts a little above 100°. It is decomposed by boiling solution of baric hydrate into acetic, succinic, and carbonic acids, and another acid not as yet examined.

DIBASIC ACIDS.

Unsaturated.

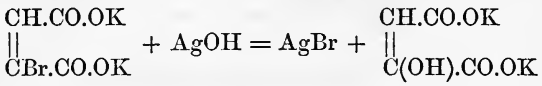
934. In some of the unsaturated dibasic acids (§ 895 and following) individual hydrogen atoms of the group C_nH_{2n-2} can be substituted by halogens by boiling the salts of the haloid additions products with water :



$$C_nH_{2n-2}Br_2(CO.ONa)_2 = NaBr + C_nH_{2n-3}Br\begin{array}{l}.CO.OH\\ .CO.ONa\end{array}$$

In this manner neutral salts of dibrom-succinic acid give salts of *brom-maleïc acid*, $C_2HBr(CO.OH)_2$, crystallising in prisms melting at 126°.

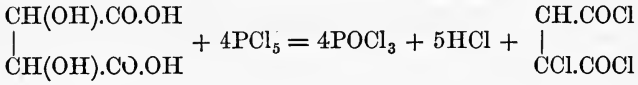
If a cold solution of the neutral potassic salt be shaken with fresh oxide of silver, bromide of silver is formed, and the potash salt of *hydroxy-maleïc acid* remains in solution :



$$\begin{array}{l}CH.CO.OK\\ \|\\ CBr.CO.OK\end{array} + AgOH = AgBr + \begin{array}{l}CH.CO.OK\\ \|\\ C(OH).CO.OK\end{array}$$

from which plumbic acetate precipitates plumbic hydroxy-maleïate, and by treatment of this in the usual way with SH_2 the free acid is obtained in easily soluble grouped feathery crystals.

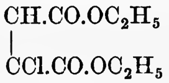
Isodibrom-succinic acid splits up by simply boiling its solution into HBr and *isobrom-maleïc acid*, very similar to its isomer, but melting at 160°. *Chlor-maleïc acid*, $C_4H_3ClO_4 = C_2HCl(CO.OH)_2$, is prepared from tartaric acid by the action of phosphoric chloride (1 part acid to 6 PCl_5), the chlor-maleïc chloride being decomposed by water :



$$\begin{array}{l}CH(OH).CO.OH\\ |\\ CH(OH).CO.OH\end{array} + 4PCl_5 = 4POCl_3 + 5HCl + \begin{array}{l}CH.COCl\\ |\\ CCl.COCl\end{array}$$

It crystallises in small needles melting at 172°.

Neutral ethyl tartrate is converted by PCl_5 into ethylic chlormaleate, an oil boiling between 250°–260° :



$$\begin{array}{l}CH.CO.OC_2H_5\\ |\\ CCl.CO.OC_2H_5\end{array}$$

Saturated Acids.

935. *Aposorbic acid*, $C_5H_8O_7 = C_3H_3(OH)_3(CO.OH)_2$, is obtained from sorbin (§ 875) by warming with nitric acid :

$$C_6H_{12}O_6 + 5O = C_5H_8O_7 + CO_2 + 2OH_2,$$

along with tartaric acid, probably formed from it by a further simultaneous oxidation :

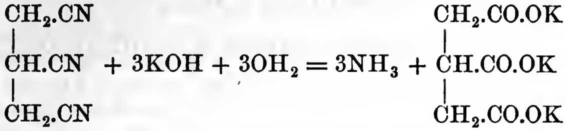
$$C_5H_8O_7 + O_2 = C_4H_6O_6 + CO_2 + OH_2.$$

Aposorbic acid generally forms irregular leafy crystals, but sometimes colourless pointed rhombohedra, dissolving in 1·63 part of water at 15° and melting at 110° with loss of water. The alkali salts are soluble; the calcium salt, $C_5H_6CaO_7 + 4OH_2$, is a white precipitate.

Tribasic Acids.

936. As yet only one acid of this group is known. *Tricarballylic* or *glyceryl tricarbonic acid* $= C_3H_5(CO.OH)_3$.

By heating glyceryl tribromide with alcohol and potassic cyanide *glyceryl tricyanide*, or tricyanhydrin, results, easily decomposable by alkalies with evolution of ammonia into an alkaline tricarballylate:



$$\begin{array}{l} CH_2.CN \\ | \\ CH.CN \\ | \\ CH_2.CN \end{array} + 3KOH + 3OH_2 = 3NH_3 + \begin{array}{l} CH_2.CO.OK \\ | \\ CH.CO.OK \\ | \\ CH_2.CO.OK \end{array}$$

It is also prepared by heating citric acid with hydriodic acid and by reduction of aconitic acid with sodium amalgam. It crystallises in colourless transparent rhombic prisms, melting at 157°-158°, and easily soluble in water, alcohol, and ether. The alkaline salts are all soluble in water; the calcium salt

$$(C_6H_5O_6)_2Ca_3 + 4OH_2,$$

is an amorphous precipitate.

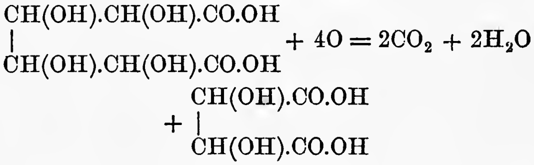
DERIVATIVES OF THE DECAVALENT HYDROCARBON NUCLEUS, C_nH_{2n-8}.

DIBASIC TETRAHYDROXY-ACIDS, $C_4H_4(OH)_4(CO.OH)_2$.

937. The isomeric acids of this group correspond to the formula $C_6H_{10}O_8$. They are obtained by the oxidation with nitric acid of the bodies of the mannite and sugar groups, $C_6H_{12}O_6$, to which they stand in the same relation as that of the dibasic acids:

$$C_nH_{2n-4}O_2(OH)_2,$$

to the divalent alcohols. By longer action of nitric acid they yield carbonic anhydride, water, and one of the modifications of tartaric acid:



$$\begin{array}{l}CH(OH).CH(OH).CO.OH\\ |\\ CH(OH).CH(OH).CO.OH\end{array} + 4O = 2CO_2 + 2H_2O + \begin{array}{l}CH(OH).CO.OH\\ |\\ CH(OH).CO.OH\end{array}$$

which is finally converted into oxalic acid.

1. *Saccharic acid* is obtained by the oxidation of mannite, cane sugar, fruit sugar, and starch. It is most conveniently prepared by heating 1 part of cane sugar with 3 parts of nitric acid of sp. gr. 1·3 until violent action commences. As soon as the evolution of red fumes ceases, the liquid is retained for a long time at a temperature of 50°, and finally diluted with several times its volume of water; it is then saturated with potassic carbonate and again over-saturated with acetic acid. On long standing the difficultly soluble hydric potassic saccharate, $C_4H_4(OH)_4\begin{matrix}.CO.OK\\ .CO.OH\end{matrix}$, crystallises in brown crusts, and is purified by recrystallisation from hot water and treatment with animal charcoal. In order to obtain the free acid, the hydric salt is neutralised with potassic hydrate and the readily soluble normal salt mixed with cadmic chloride solution. The insoluble cadmic saccharate is then washed, suspended in water, decomposed by hydric sulphide, and the filtrate evaporated.

Saccharic acid so obtained forms a gum-like, deliquescent mass; it is soluble in alcohol, and begins to decompose, with brown coloration, at a little above 100°.

The salts of saccharic acid resemble those of tartaric acid; the hydric potassic and ammonic salts are difficultly soluble, the normal alkaline salts readily soluble and deliquescent; most other metals yield salts difficultly soluble or insoluble in water.

Ethylic saccharate, $C_4H_4(OH)_4(CO.O.C_2H_5)_2$, is crystalline, but is difficult to obtain in a state of purity; it forms a crystalline compound with calcic chloride, $2C_{10}H_{18}O_8,CaCl_2$, which reacts with chlor-acetyl, yielding *ethylic tetraceto-saccharate*, $C_4H_4(O.C_2H_3O)_4(CO.O.C_2H_5)_2$, forming tabular crystals, melting at 61°, insoluble in water, but soluble in alcohol and ether.

2. *Mucic Acid.*—This acid, isomeric with the preceding, is obtained by the oxidation of dulcite, lactose, arabine, vegetable mucilage, and also, together with saccharic acid, from milk sugar and melitose. Usually 1 part of finely powdered milk sugar is gently heated with 3 parts of nitric acid of sp. gr. 1·3 until the stormy evolution of red fumes ensues, and the reaction then allowed to complete itself; a white sandy powder of mucic acid separates, which is purified by well washing with water.

Mucic acid is nearly insoluble in cold water and alcohol, only difficultly soluble in boiling water. The greater part of its salts are insoluble, even the normal potassic and ammonic salts being difficultly soluble, whilst the hydric potassic salt is somewhat more readily soluble.

Ethylic mucate, $C_6H_8(C_2H_5)_2O_8$, crystallising in four-sided prisms, melting at 158°, is obtained by heating mucic acid with four parts of sulphuric acid and four parts of alcohol. It dissolves readily in water and alcohol at the boiling temperature. Heated with chlor-acetyl it is converted into *ethylic tetraceto-mucate*, which is readily soluble in hot alcohol, crystallises in fine glassy needles, melts at 177°, and begins to sublime at 150°.

Phosphoric chloride converts mucic acid into the crystalline chlor-muconic acid dichloride, $C_6H_2Cl_4O_2$:

$$C_4H_4(OH)_4(CO.OH)_2 + 6PCl_5 = 6POCl_3 + 8HCl + C_4H_2Cl_2(CO.Cl)_2,$$

which is converted by water into the dibasic *chlor-muconic acid:*

$$C_4H_2Cl_2(CO.Cl)_2 + 2H_2O = 2HCl + C_4H_2Cl_2(CO.OH)_2.$$

This is difficultly soluble in cold water, and can be obtained crystalline from a hot saturated solution. Sodium amalgam and water convert it into hydromuconic acid (§ 898).

By heating at 180° with much fuming hydriodic acid mucic acid is reduced to adipic acid (§ 839):

$$C_4H_4(OH)_4(CO.OH)_2 + 8HI = 4I_2 + 4H_2O + C_4H_8(CO.OH)_2.$$

When mucic acid is boiled for a long time with water, and the clear solution evaporated to dryness on the water bath, a third isomeride,

3. *Paramucic acid*, is obtained, which dissolves in 5·8 parts of hot and about 70 parts of cold water, and is somewhat more soluble in alcohol. It is very readily converted into mucic acid, e.g. by cooling the hot saturated aqueous solution.

Compounds of the Pyromucic Acid Group.

938. By dry distillation of mucic and paramucic acids two isomeric monobasic acids of the formula $C_5H_4O_3$ are obtained—

pyromucic and isopyromucic acids, whose constitutions are not yet clearly known. The same holds good for the reaction products of the pyromucic acids and their aldehyde, furfurol, so that these compounds, though derivatives of different hydrocarbon radicals containing the same carbon nucleus, are considered in connection with mucic acid.

Pyromucic acid, $C_5H_4O_3$, is prepared from the liquid passing over in the dry distillation of mucic acid, by neutralisation with sodic hydrate, evaporation of the filtrate to a small volume, acidulation of the residue with sulphuric acid, and shaking out with ether. The ethereal solution, on evaporation, leaves a mixture of the two isomeric pyromucic acids, which are separated by means of a small quantity of cold water.

Pyromucic acid can also be obtained by boiling its aldehyde with water and argentic oxide; it crystallises in colourless needles or prisms, melts at 134 and sublimes below this temperature. It dissolves readily in alcohol and in 4 parts of boiling and 28 parts of cold water. Its alkali salts, e.g. $C_5H_3KO_3$, are readily soluble and crystallise with difficulty.

Ethylic pyromucate, $C_5H_3(C_2H_5)O_3$, crystallises in leaves, melting at 34° and boiling at 208°–210°. It unites directly with chlorine, forming the liquid tetrachloride, $C_5H_3Cl_4(C_2H_5)O_3$, and reacts with ammonia, forming the crystalline *pyromucamide*, $C_5H_3O_2.NH_2$. Phosphoric pentachloride yields with pyromucic acid the *chloride* $C_5H_3O_2.Cl$, an oil boiling at 170°. This chloride, as also the fact that ethylic pyromucate is *not* affected by chlor-acetyl, are in opposition to the former view that pyromucic acid was a hydroxy-acid of the formula $C_4H_2(OH).CO.OH$. One oxygen atom appears more probably to be united to the nucleus in anhydro fashion, so that, in lack of a detailed constitutional formula, the expression $C_4H_3(O).CO.OH$ seems the best.

Isopyromucic acid, $C_5H_4O_3$, dissolves very readily in cold water; it melts at 82° and commences to sublime below 100° in colourless plates, which soon turn yellow in air.

Both acids are formed according to the equation:

$$C_4H_4(OH)_4.(CO.OH)_2 = CO_2 + 3H_2O + C_4H_3O.CO.OH.$$

By evaporation of a solution of pyromucic acid with a moderate amount of bromine fumaric acid is formed:

$$C_5H_4O_3 + 3Br_2 + 3H_2O = C_4H_4O_4 + CO_2 + 6HBr;$$

by employment of more bromine *mucobromic acid*, $C_4H_2Br_2O_3$, is obtained, which crystallises well.

939. *Pyromucic aldehyde*, or *furfurol*, $C_5H_4O_2 = C_4H_3(O).CH:O$. Furfurol occurs amongst the products of the dry distillation of sugar, and is obtained by heating bran, meal, or sawdust with dilute sulphuric acid or zincic chloride solution. It is usually prepared by distilling two parts of wheat bran with one part of sulphuric acid previously diluted with double its weight of water, the distillate being neutralised with potassic hydrate and rectified. Furfurol passes over with the aqueous vapour as a colourless oil of sp. gr. 1·165 and boiling at 163°. Exposed to air, it turns brown and finally becomes a tar-like mass. It requires twelve times its weight of water for solution and mixes with alcohol in every proportion.

As a true aldehyde furfurol is converted into pyromucic acid by boiling with water and argentic oxide, and it also enters into combination with hydric alkali sulphites. Hydric sulphide converts it into *thio-furfurol*, C_5H_4OS, a white crystalline powder; with ammonia it reacts according to the equation:

$$3C_4H_3(O).CH:O + 2NH_3 = 3H_2O + [C_4H_3(O).CH:]_3N_2,$$

forming furfuramide. *Furfuramide* forms neutral, colourless crystals, insoluble in water, but soluble in alcohol. On heating to 120° or by boiling with potassic hydrate solution it is converted into the isomeric base *furfurine*, $C_{15}H_{12}O_3N_2$, which crystallises in silky needles, is somewhat soluble in water, more readily so in alcohol, and forms crystalline salts with acids, e.g. $C_{15}H_{12}N_2O_3,HCl,H_2O$.

Furfurylic alcohol, $C_5H_6O_2 = C_4H_3O.CH_2.OH$. On mixing furfurol with alcoholic potassic hydrate, heat is evolved, and on cooling the liquid solidifies to a crystalline mass, from which ether extracts furfurylic alcohol:

$$2C_5H_4O_2 + KOH = \underset{\text{Potassic pyromucate.}}{C_5H_3KO_3} + \underset{\text{Furfurylic alcohol.}}{C_5H_6O_3}.$$

Furfurylic alcohol is a liquid which readily turns brown from oxidation on exposure to air; it distils between 170° and 180°, readily decomposing into water and a thick brown oil during the distillation. Acids convert it into a red resin.

940. On submitting ammonic pyromucate to dry distillation an oily and an aqueous distillate is obtained. The oil consists mainly of *pyrrol*, $C_4H_5N = C_4H_3(NH)H$, which is obtained colourless on rectification and boils at 133°; it soon turns brown on exposure to air. By heating with acids it is converted into orange-coloured or red flocks of *pyrrol red*.

The aqueous layer of the distillate, on evaporation, yields crystals of

Carbo-pyrrol amide, $C_5H_6ON_2 = C_4H_3(NH).CO.NH_2$, melting at 173° and decomposed on boiling with strong mineral bases into ammonia and

Carbo-pyrrolic acid, $C_5H_5O_2N = C_4H_3(NH).CO.OH$. This latter crystallises in small prisms subliming at 190°, and decomposing at higher temperatures into carbonic anhydride and pyrrol:

$$C_5H_5O_2N = CO_2 + C_4H_5N.$$

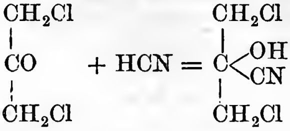
By distilling pyromucates with soda lime some quantities of a liquid, *tetraphenol*, are obtained, which is colourless, neutral, boils at 32°, and has the formula C_4H_4O.

TRIBASIC HYDROXY-ACIDS.

Citric Acid, $C_6H_8O_7 = C_3H_4(OH)(CO.OH)_3$.

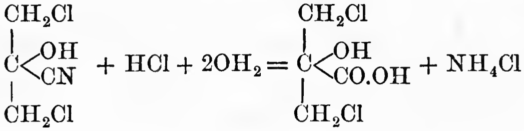
941. Citric acid occurs in the free state in lemons and other acid fruits, such as gooseberries, currants; in the form of salts in the beet root, the tubers of *Helianthus tuberosus*, the leaves of *Cerasis acida*, the bark of *Aesculus Hippocastanum*, &c. On the large scale it is prepared from lemons, the expressed juice being cleared by boiling with albumin and then saturated whilst hot with powdered chalk and milk of lime. The precipitated normal calcic citrate is decomposed by the equivalent quantity of sulphuric acid, and the liquid filtered from the gypsum and evaporated to dryness.

Citric acid has been obtained synthetically from symmetrical dichlor acetone (§ 768) by the following series of reactions. The dichlor acetone is first heated with strong hydrocyanic acid:



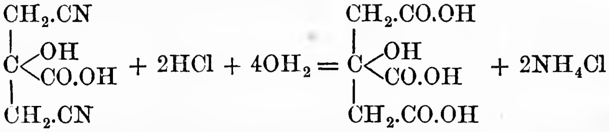
$$\begin{array}{c}CH_2Cl\\ |\\ CO\\ |\\ CH_2Cl\end{array} + HCN = \begin{array}{l}CH_2Cl\\ |\\ C{<}\begin{smallmatrix}OH\\ CN\end{smallmatrix}\\ |\\ CH_2Cl\end{array}$$

The resulting cyano-hydrate is then boiled with hydrochloric acid:



$$\begin{array}{l}CH_2Cl\\ |\\ C{<}\begin{smallmatrix}OH\\ CN\end{smallmatrix}\\ |\\ CH_2Cl\end{array} + HCl + 2OH_2 = \begin{array}{l}CH_2Cl\\ |\\ C{<}\begin{smallmatrix}OH\\ CO.OH\end{smallmatrix}\\ |\\ CH_2Cl\end{array} + NH_4Cl$$

The dichlor-acetonic acid formed, when treated with KCN, exchanges its chlorine for cyanogen, and the resulting cyanide, when boiled with hydrochloric acid, yields citric acid:



$$\begin{array}{l}CH_2.CN\\ |\\ C{<}\begin{smallmatrix}OH\\ CO.OH\end{smallmatrix}\\ |\\ CH_2.CN\end{array} + 2HCl + 4OH_2 = \begin{array}{l}CH_2.CO.OH\\ |\\ C{<}\begin{smallmatrix}OH\\ CO.OH\end{smallmatrix}\\ |\\ CH_2.CO.OH\end{array} + 2NH_4Cl$$

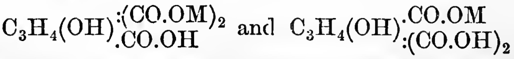
Citric acid crystallises in large colourless rhombic prisms of strongly acid taste, of the formula $C_6H_8O_7,H_2O$; they melt at 100°, but only lose water at a higher temperature. Citric acid is soluble in water and alcohol, but scarcely in ether.

On heating to 175° citric acid loses water and is converted into *aconitic acid*, $C_3H_3(CO.OH)_3$, which at higher temperatures decomposes into carbonic anhydride and itaconic acid. On fusing with excess of an alkali citric acid yields salts of oxalic and acetic acids:

$$C_6H_5K_3O_7 + KOH = K_2C_2O_4 + 2KO.C_2H_3O.$$

Mould soon developes in aqueous solutions of citric acid, under whose influence the acid is rapidly decomposed.

As a tribasic acid citric acid yields three classes of salts, normal, $C_3H_4(OH)(CO.OM)_3$, and two acid:



$$C_3H_4(OH)\begin{smallmatrix}:(CO.OM)_2\\ .CO.OH\end{smallmatrix} \text{ and } C_3H_4(OH)\begin{smallmatrix}.CO.OM\\ :(CO.OH)_2\end{smallmatrix}$$

Potassic Salts.—By saturating citric acid with potassic hydrate or carbonate, tripotassic citrate, $C_6H_5K_3O_7,H_2O$, is obtained in colourless needles, which are deliquescent and are insoluble in alcohol. On mixing a solution of two molecules of this with one molecule of citric acid and evaporating, *dipotassic citrate*, $C_6H_6K_2O_7$, is obtained as an amorphous, readily soluble mass; whilst mixed solutions of one molecule of the tribasic salt with two molecules of citric acid yield *monopotassic citrate,* $C_6H_7KO_7,H_2O$, large colourless prisms, soluble in alcohol.

Calcic citrate, $(C_6H_5O_7)_2Ca_3,4H_2O$, is more soluble in cold water than in hot, and dissolves readily in hydrochloric or acetic acids. The acid salts are obtained by addition of the necessary quantities of citric acid, and are readily soluble. $C_6H_6CaO_7,H_2O$ crystallises in brilliant plates; $(C_6H_7O_7)_2Ca$ generally forms a gummy mass, only obtained crystalline with difficulty.

Argentic citrate, $C_6H_5O_7Ag_3$, is obtained by double decomposition of argentic nitrate and trialkaline citrates, as a white flocculent precipitate, which dissolves in boiling water (invariably with partial decomposition) and separates in crystals on cooling.

Triethylic citrate is obtained by a similar method to that for ethylic malate (§ 904) and tartrate (§ 861). It is a liquid of oily consistence and is somewhat soluble in water. It decomposes on distillation, and on treatment with chlor-acetyl yields *triethylic acetocitrate,* insoluble in water and boiling at 288°:

$$\begin{aligned} &C_3H_4(OH)(CO.O.C_2H_5)_3 + Cl.C_2H_3O \\ &= C_3H_4(O.C_2H_3O)(CO.O.C_2H_5)_3 + HCl. \end{aligned}$$

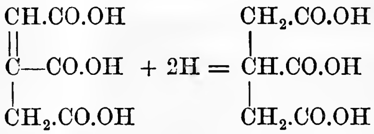
Ammonia converts it into crystalline citramide:

$$C_3H_4(OH)(CO.NH_2)_3,$$

which is difficultly soluble in water.

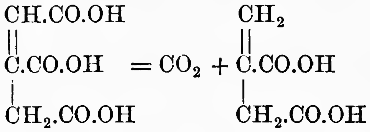
DERIVATIVES OF RADICALS POORER IN HYDROGEN.

942. *Aconitic acid*, $C_6H_6O_6 = C_3H_3(CO.OH)_3$, occurs in the form of calcic salt in various species of *aconitum*, also in *Delphinium Consolida* and *Equisetum fluviatile*. It can be obtained from citric acid, with elimination of water, by heating at 175° or by long heating with concentrated hydrochloric or hydrobromic acids at 140°. It is best prepared by heating citric acid in a retort until oily streaks are observed on the neck, when the residue is cooled and extracted with ether. It crystallises in white plates or granules, soluble in water, alcohol, and ether, and melts at 140°. It is a tribasic acid and unites with nascent hydrogen, forming tricarballylic acid (§ 936):



$$\begin{array}{lcl} \mathrm{CH.CO.OH} & & \mathrm{CH_2.CO.OH} \\ \| & & | \\ \mathrm{C{-}CO.OH} & +\ 2\mathrm{H} = & \mathrm{CH.CO.OH} \\ | & & | \\ \mathrm{CH_2.CO.OH} & & \mathrm{CH_2.CO.OH} \end{array}$$

and on dry distillation yields itaconic acid (§ 897, 1):



$$\begin{array}{lcl} \mathrm{CH.CO.OH} & & \mathrm{CH_2} \\ \| & & \| \\ \mathrm{C.CO.OH} & = \mathrm{CO_2} + & \mathrm{C.CO.OH} \\ | & & | \\ \mathrm{CH_2.CO.OH} & & \mathrm{CH_2.CO.OH} \end{array}$$

The *normal calcic salt*, $(C_6H_3O_6)_2Ca_3,6H_2O$, crystallises in prisms and is difficultly soluble.

Aceconitic acid, whose ethylic salt is formed in the decomposition of ethylic brom-acetate with sodium, is probably an isomer of aconitic acid.

943. *Meconic acid*, $C_7H_4O_7$, occurs in the milky juice of poppies and in the opium prepared therefrom, and passes into the alcoholic extract of the latter. From this baric chloride precipitates baric meconate nearly in a state of purity, the free acid being obtained by addition of sulphuric acid; it is then converted into the ammonic salt, and this recrystallised several times from hot water and finally decomposed by hydrochloric acid.

Meconic acid crystallises in colourless, mica-like plates or prisms containing three molecules of water, which is given off at 100°. It is difficultly soluble in cold water or ether, more readily in hot water and alcohol. The alkali and ammonium salts are readily soluble, all others difficultly soluble or insoluble. The above-mentioned *baric salt* has the formula $C_7H_2BaO_7,H_2O$. *Calcic meconate:*

$$C_7H_2CaO_7,H_2O,$$

dissolves in warm nitric acid, the solution on cooling yielding brilliant plates of the *monobasic salt* $(C_7H_3O_7)_2Ca,2H_2O$. Two *silver salts* are known, a white, $C_7H_2Ag_2O_7$, and a yellow, $C_7HAg_3O_7$, only obtainable by aid of an ammoniacal solution of argentic nitrate. Meconic acid yields a most intense blood-red coloration with ferric chloride.

On saturating an alcoholic solution of meconic acid with hydrochloric acid gas, and cooling, feathery crystals of *hydric ethylic meconate*, $C_7H_3(C_2H_5)O_7$, separate, and on evaporation of the mother liquor *diethylic meconate*, $C_7H_2(C_2H_5)_2O_7$, is obtained as an oily liquid which solidifies in crystals.

Sodium amalgam and water convert meconic acid, with union of six hydrogen atoms, into *hydromeconic acid*, $C_7H_{10}O_7$.

944. By long boiling with water, or better dilute hydrochloric acid, or by heating alone to 200°, meconic acid gives off carbonic anhydride:

$$C_7H_4O_7 = CO_2 + C_6H_4O_5,$$

and is converted into *comenic acid*, which crystallises in hard granules or plates, is difficultly soluble, and readily yields salts containing one equivalent of metal, $C_6H_3MO_5$. Compounds of the formula $C_6H_2M_2O_5$ are only obtained in the presence of much free ammonia. The only ethylic salt, $C_6H_3(C_2H_5)O_5$, crystallises in needles melting at 135°. On dry distillation comenic acid splits up into carbonic anhydride and *pyrocomenic acid:*

$$C_6H_4O_5 = CO_2 + C_5H_4O_3,$$

which, however, can scarcely be termed an acid, as it crystallises unchanged from a hot solution of potassic hydrate. Metallic derivatives, such as $(C_5H_3O_3)_2Ca,H_2O$ and $C_5H_3AgO_3$, can only be obtained in the presence of much free ammonia by addition of the acetates of calcium, barium, and lead, or of argentic nitrate. Ethylic derivatives have not been obtained.

From these properties meconic acid would appear to be a dibasic hydroxy-acid, $C_5HO_2(OH)(CO.OH)_2$, comenic acid:

$$C_5H_2O_2(OH).CO.OH,$$

and pyrocomenic acid, $C_5H_3O_2.OH$. Nothing is known of the inner constitution of these bodies.

945. *Chelidonic acid*, $C_7H_4O_6$, is obtained from the sap of *Chelidonium majus*, by slightly acidulating with nitric acid, precipitating with plumbic acetate, and decomposing the resulting lead salt with hydric sulphide. It crystallises in silky needles containing one molecule of water of crystallisation, difficultly soluble in cold water or alcohol. It decomposes at 220° with evolution of carbonic anhydride. It yields salts containing three equivalents of metals; they are of a yellow colour, and, with exception of the alkali salts, insoluble in water. The hydric salts are colourless, like the acid, and are mostly crystalline.

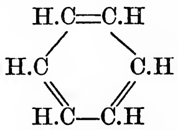
AROMATIC COMPOUNDS.

946. The term '*aromatic compounds*' has been applied to a large class of bodies derived more or less directly from benzene, C_6H_6, by the substitution of one or more of its hydrogen atoms by other elements or compound radicals, similarly to the bodies of the fatty or alkyl series which are derived from marsh gas or methane, CH_4 (§ 141, &c.)

The term aromatic was applied at a time when fewer benzene derivatives were known than at present, and on the supposition that the presence of the benzene nucleus in any body accounted for the more or less strongly pronounced aromatic odour possessed by these bodies; and in this work the term is used generally to indicate that the body contains the benzene nucleus, whether it be derived from benzene by substitution of an alkyl group or from the introduction of a benzene group into a body belonging to the fatty series.

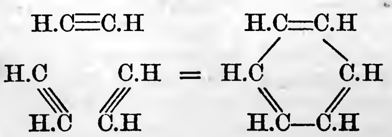
947. Various theories have been proposed as to the constitution of the benzene nucleus. The one which has perhaps been most fruitful in results, and best supported by facts, is that proposed in 1865 by Kekulé, according to which the benzene nucleus must be considered as *a ring or closed chain* of carbon atoms, combined to each other with alternating single and double union, and so that each carbon atom is combined with one hydrogen atom only.

This may be expressed in one plane thus:



Several important facts seem to support this theory of its constitution.

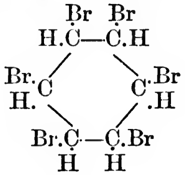
1. The synthesis of benzene from acetylene, by passing that gas through a red-hot tube, when it may be supposed to combine:



2. The power which benzene possesses of combining with two, four, or six atoms of bromine or chlorine to form so-called 'additive' compounds, behaving towards the halogens in this respect like three molecules of a compound each of which possesses a double carbon combination.

The fact that not more than six atoms of chlorine or bromine can be combined with benzene is a decided indication of a *closed* chain form of combination of the carbon atoms; for in the case of an open chain a compound of six carbon with six hydrogen atoms would be able to combine with eight atoms of chlorine or bromine, as in the case of the only known isomer of benzene, dipropargyl (§ 932), which combines with eight atoms of bromine.

In these additive compounds of benzene with monad elements the divalent unions are supposed to be changed into monovalent, the closed formation of the group still being maintained:



The comparative instability of these compounds also supports the above view of their constitution.

3. Many benzene derivatives, especially the benzene carboxylic acids, $C_6H_4(CO.OH)_2$, $C_6(CO.OH)_6$, &c., are acted upon by nascent hydrogen, of which up to six atoms may be united, and frequently can be again removed by chlorine or oxidising agents, with regeneration of the original acid.

On the other hand, if eight hydrogen atoms are added to a saturated aromatic compound, which can be effected in some cases by heating to about 200° with concentrated hydriodic acid, derivatives of the paraffin series are obtained, which no longer possess the character of aromatic compounds and cannot be converted into benzene or benzene derivatives by simple means.

4. The six hydrogen atoms in benzene all appear to possess the same value; in cases where only one hydrogen atom in benzene is replaced by an element or compound radical it is a matter of perfect indifference which atom is replaced, the mono-substituted compound obtained having exactly the same properties, although prepared by methods differing so as to ensure that different hydrogen atoms should be replaced in each case. *No isomeric monosubstituted benzenes have been obtained.*

948. *Chemical Character of the Benzene Nucleus.*—Substituted products are somewhat easily obtained from benzene and such of its derivatives as still contain some hydrogen atoms in connection with the benzene nucleus, by the action of the halogens, nitric acid, sulphuric acid, &c., in the case of the two last-mentioned bodies much more readily than with compounds of the 'alkyl' series.

The peculiarities of the benzene group itself are exhibited in all its derivatives, especially in some of its hydroxyl, nitro, and amido compounds.

The hydroxyl substitution products or hydrates of this series correspond in many respects to the alcohols, only that the hydroxylic hydrogen is much more readily replaced by basic metals. Barium, calcium, or alkali metal compounds may be obtained from monhydroxy-benzene, or phenol, $C_6H_5.OH$, by mixing it with aqueous solutions of the respective bases and evaporating. And it is from this readiness which phenol exhibits to form compounds with strong bases that it obtained the name *carbolic acid*, although it has no real acid nature, for its basic compounds are easily decomposed by carbonic acid with reproduction of phenol:

$$2C_6H_5.ONa + OH_2 + CO_2 = Na_2CO_3 + 2C_6H_5.OH.$$

The hydrates of the benzene nucleus occupy electro-chemically a position *between* the alcohols or carbinols and the acids proper, and are termed 'phenols.' When, however, several hydrogen atoms in benzene are substituted by hydroxyl, or by hydroxyl and nitryl or halogens, the products are of decidedly acid character.

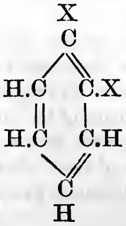
The peculiar chemical properties of the benzene group are also exhibited in its amido derivatives. In the case of alkylamines (§ 264), produced by the substitution of the ammonic hydrogen atoms in ammonia by alcohol radicals, the basic character is intensified by each such substitution, $C_2H_5.NH_2$ being more positive than NH_3, and so on. But in the benzene amides the reverse is the case. Aniline, phenylamine, $C_6H_5.NH_2$, for instance, will form comparatively stable salts; the salts of diphenylamine, $(C_6H_5)_2NH$, are decomposed by water, and triphenylamine, $(C_6H_5)_3N$, does not combine with acids.

949. *Isomerism in the Polysubstituted Products of Benzene.*—Most important support is given to the above view of the constitution of benzene by the study of the isomeric bodies produced by the substitution of several hydrogen atoms in the benzene nucleus, the differences in physical and chemical properties being referable, as also in the case of ethane derivatives, to the relative position of the substituting groups to each other.

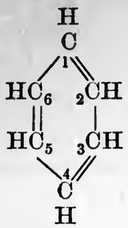
The simplest products result when the substituting elements or radicals are the same.

950. If two hydrogen atoms in benzene be substituted by the same element or compound radical three cases of isomerism arise, depending on the relative position of these substituting elements or radicals.

1. If the substitution take place at neighbouring carbon atoms, *ortho derivatives* are produced, thus:



If, for convenience of reference, the carbon atoms be numbered:

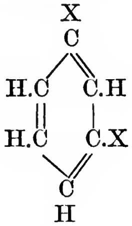


then these *ortho* derivatives may be designated by the figures

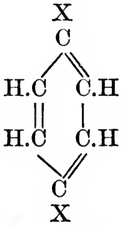
$$X:X = 1:2$$

or by any other two consecutive numbers.

2. If one CH group be situated between the carbon atoms at which substitution has taken place, the products are termed *meta* derivatives, and may be represented by the convention of numbering thus: $X:X = 1:3$ or $1:5$:



3. When the substitution takes place at those carbon atoms supposed to be farthest removed from each other bodies of the *para* series result: $X:X = 1:4$:



In such bodies two CH groups occupy positions between the carbons at which substitution has taken place.

It was assumed by Kekulé that the positions represented by the numbers 1 and 2 were identical with 1 and 6, and so on; so that only three isomers of a disubstituted benzene could exist. The identity of these positions has, however, been disputed, for it will be observed in the figure that in one case the carbon atoms are united by double bonds and in the other by single only, and if this could cause any physical or chemical difference four isomeric modifications of disubstituted benzenes should exist; but direct experiments appear to show that if a substance has been prepared by methods so devised as to lead to the two replacing groups occupying the positions 1 : 2 and 1 : 6 respectively, the body obtained by both methods is identical.

951. In the case of the trisubstitution derivatives of benzene, where the substituting agent is the same, only three isomers are possible.

1. One product with neighbouring positions :

1 . 2 . 3.

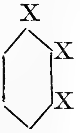
2. One product with two positions adjacent :

1 . 2 . 4.

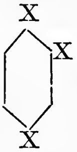
3. One product not containing neighbouring positions :

1 . 3 . 5.

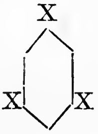
It has been proposed to term these three isomeric forms consecutive, unsymmetrical, and symmetrical, the meaning of these terms being clearly shown by the formula given below :



Consecutive.



Unsymmetrical.



Symmetrical.

In these abridged formulæ, which are frequently used, the hexagon represents the benzene nucleus, i.e. the six carbon atoms, and such hydrogen atoms as are still unreplaced.

It is more complicated when only two of the three substituting elements or radicals are alike, e.g. $C_6H_3X_2Y$, and still more so when all three are unlike, e.g. $C_6H_3.X.Y.Z$.

In the latter case no less than ten isomers must occur, the positions 1 . 2 . 3 giving three isomers in the order X.Y.Z., X.Z.Y., Y.X.Z., whilst 1 . 2 . 4 would give six isomers in the order X.Y.Z., X.Z.Y., Z.Y.X., Z.X.Y., Y.Z.X., and Y.X.Z., and 1 . 3 . 5 would correspond to only one isomer.

952. Four similar groups or elements substituting in benzene give rise to the same number of isomers as with the disubstitution products, for $C_6H_2X_4$ and $C_6H_4X_2$ have the same relation to each other.

The isomers would be 1 : 2 : 3 : 4, 1 : 2 : 4 : 5, and 1 : 3 : 4 : 5.

The same relationship exists between the penta-substituted and mono-substituted benzenes :

$$C_6HX_5 \text{ and } C_6H_5X,$$

so that only one modification can exist, and so likewise with a completely substituted benzene, C_6X_6, as long as the replacing elements or groups are similar. Very complicated cases of isomerism arise where in poly-substituted benzenes all the entering radicals are dissimilar ; and in these cases the individual isomers are the more difficult to separate and distinguish the greater their number, in consequence of slighter differences in chemical and physical character ; so that the investigation of these relationships is confined within very narrow limits.

953. *Increase in Number of Isomers by Substitution in Side Chains.*—By substituting hydrocarbons for the hydrogen in benzene a much greater number and variety of isomeric bodies may be obtained, since, in addition to the benzene hydrogen atoms, the hydrogen of the substituting hydrocarbon groups may be replaced.

With methyl benzene or toluene, for instance, the substitution may take place either in the benzene nucleus, $C_6H_4X.CH_3$, or in the methyl, $C_6H_5.CH_2.X$, and so on.

Determination of Position Isomers in the Benzene Nucleus.

954. The determination of the places or points of substitution in poly-substitution derivatives of benzene has been carried out with considerable certainty, mostly with di-derivatives and to a less extent with tri-derivatives.

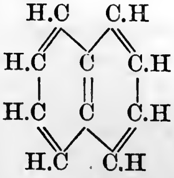
Some few only of the leading arguments concerning the determination of these points of substitution in benzene derivatives can be given here.

As mono-substitution products give no isomers, and di-substitution products at most three, it is only necessary to determine to which series, ortho, meta, or para, the derivative body belongs.

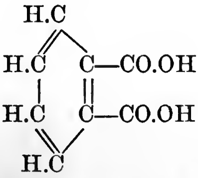
The most general reference in use with respect to di-derivatives of benzene has been to the constitution of the three isomeric benzene dicarboxylic acids, $C_6H_4\begin{matrix}.CO.OH\\.CO.OH\end{matrix}$, phthalic, isophthalic, and terephthalic acids, the first being considered as in the ortho position $= 1:2$; the second as meta, $1:3$; and the last as the para compound, $1:4$; and, so far as it has been possible to convert any other di-substitution product of benzene into any one of these acids by any moderately easy and direct process, these compounds have been looked upon as belonging to the same series, ortho, meta, para, as the case might be.

But this method is not always reliable or definite, as it happens sometimes that the same body will, after treatment and passing through various intermediate compounds and stages, give more than one acid of the formula $C_6H_4:(CO.OH)_2$, this being especially the case when very high temperatures have been employed, under the influence of which, as has been proved, one isomeric state may change or pass into another of a more stable kind under those conditions.

A strong argument for the assignment of the ortho position to phthalic acid is its production from naphthalene, $C_{10}H_8$, by oxidation. The probable constitution of this body, and the resulting phthalic acid, according to Græbe, is:



Naphthalene.



Phthalic acid.

This view of the constitution of phthalic acid is also supported by the fact that it alone of the three benzene dicarboxylic acids yields an anhydride, $H_4C_6\begin{matrix}(C=O)\\(C=O)\end{matrix}>O$, by simply heating, in an analogous manner to maleïc and succinic acids, and again by the ease with which it is totally oxidised to water and carbonic acid by chromic acid.

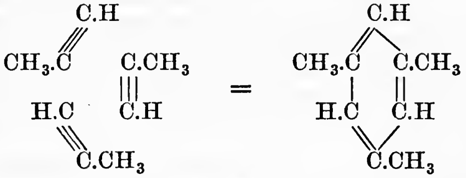
This last property seems especially to characterise ortho compounds in which the substituting groups already contain oxygen or hydrocarbon radicals.

It appears, indeed, to be a general fact that oxidation takes place with the greatest ease at those carbon atoms or groups to which oxygen or carboxyl groups are already attached, and especially also when at the same time the neighbouring carbon atoms are connected by divalent union, as in this case.

The *meta position* is assigned to the carboxyl group in isophthalic acid on account of its derivation from mesitylene, $C_6H_3.(CH_3)_3$. This body results from the abstraction of three molecules of water from three molecules of acetone, $CH_3.CO.CH_3$, under the influence of sulphuric acid, and similarly from three molecules of allylene.

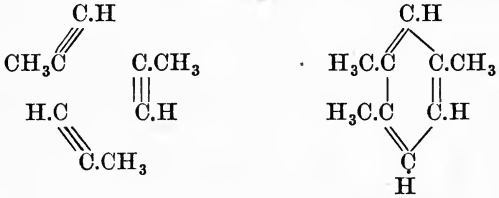
In the latter case the process may be thus represented :

1.



or,

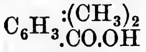
2.



Mesitylene.

Of the two, 1 seems the most rational, as in this case each of the three acetone molecules behaves in a similar manner, the product being therefore symmetrical as expressed by the position numbers 1 : 3 : 5 ; and, further, it has been shown that all three hydrogen atoms still attached to the benzene nucleus have the same value, i.e. in the case of mono-substitution products it is a matter of indifference which hydrogen atom is substituted ; this would only be the case with a body of the first formula.

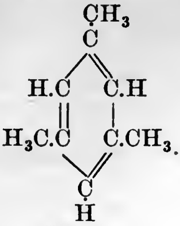
By gentle oxidation mesitylene yields mesitylenic acid :



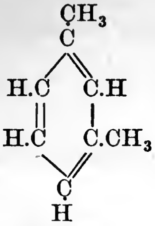
$$C_6H_3\begin{matrix}:(CH_3)_2\\.CO.OH\end{matrix}$$

which on distillation with calcic hydrate splits up into carbonic acid and a dimethyl benzene, or isoxylene, $C_6H_4 : (CH_3)_2$, in which, from the method of its production, the two methyl groups occupy the positions 1 : 3.

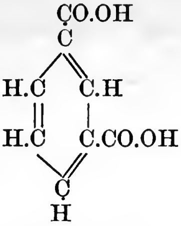
According to the first of the above formulæ of mesitylene, isoxylene can only have this meta constitution, and therefore the isophthalic acid obtained from it by oxidation is considered to be benzene meta-dicarboxylic acid. These relations may perhaps be better seen by comparing the three formulæ:



Mesitylene.



Isoxylene.

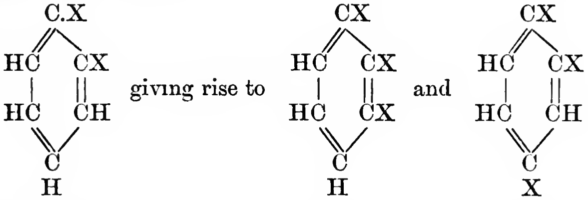


Isophthalic acid.

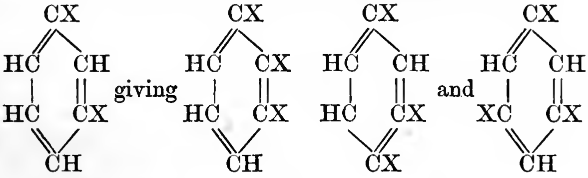
If the above deductions be correct terephthalic acid can only occupy the remaining or *para position* in the benzene nucleus.

954*a*. A further method of determining the relative positions to be assigned to the various replacing elements or groups in the disubstitution derivatives of benzene has lately been devised by Körner, which is free from the objections raised against the previous methods, inasmuch as high temperatures are not employed. It consists in determining the number of tri-substitution derivatives that can be derived from or converted into any di-substitution derivative of benzene.

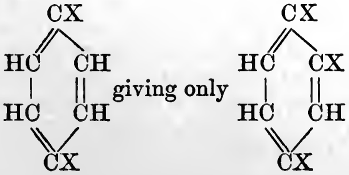
In the case of an ortho compound it will be possible to obtain *two* isomeric tri-derivatives:



A meta compound can yield *three* isomeric tri-derivatives:



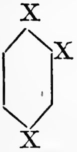
whilst with a para compound only a *single* tri-derivative can be obtained:



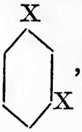
In those cases where the fresh substituting group or element was identical with that already occurring in the di-derivative the consecutive tri-derivative 1 : 2 : 3 = 

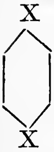
could be obtained from both the ortho 

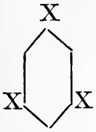
and meta 

di-derivatives; the unsymmetrical or 1 : 2 : 4 tri-derivative 

is obtained from the ortho 

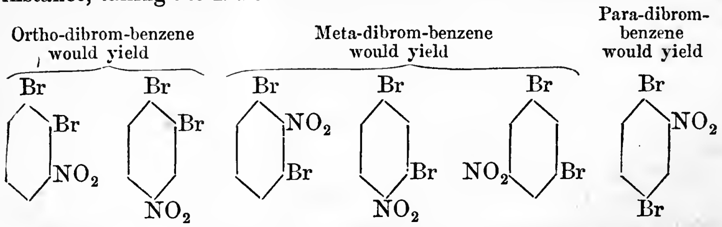
, meta 

, and para 

di-derivatives and, finally, the symmetrical tri-derivative 

can only be obtained from the meta di-derivative 

In those cases, on the other hand, where the third replacing group is different from that occurring in the di-derivative, and where, therefore, six tri-derivatives are possible, these bodies would be all different. For instance, taking the nitro-dibrom benzenes :



This has been carefully worked out for the dibrom-benzenes, and it is further found that dibrom-benzene which gives only a single tri-derivative can be converted by simple means into terephthalic acid, and similarly that the dibrom-benzene giving rise to three tri-derivatives is convertible into isophthalic acid, thus fully corroborating the previous ideas that terephthalic acid was a para (1 . 4) compound, isophthalic a meta (1 . 3) compound, and leaving the ortho (1 . 2) as the only position for phthalic acid.

BENZENE AND ITS SUBSTITUTION DERIVATIVES BY CARBON FREE RADICALS.

Benzene, C_6H_6.

955. Benzene is obtained synthetically by passing acetylene through tubes heated to whiteness (§ 947, 1), and this probably explains its occurrence amongst the fluid products of the dry distillation of many organic bodies. Many dense hydrocarbons and homologues of benzene also yield that body on exposure to a very high temperature, which may possibly account for its presence in coal-tar oil along with many of its homologues, with phenols, aniline, pyridine bases, and solids like naphthalene, anthracene, phenanthrene, &c.

Chemically pure benzene may be prepared by carefully distilling calcic benzoate or benzoic acid with quick-lime:

$$C_6H_5.CO.OH + CaO = CaCO_3 + C_6H_6,$$

and similarly by distilling the polybasic benzoic acids with excess of calcic oxide, e.g.

$$C_6H_3(CO.OH)_3 + 3CaO = 3CaCO_3 + C_6H_6;$$

also by passing its hydroxyl substitution derivatives over strongly heated zinc dust:

$$C_6H_5.OH + Zn = ZnO + C_6H_6.$$

On the manufacturing scale benzene is always obtained from the coal-tar oil boiling below 100°.

Coal tar is separated by distillation into three principal fractions.

1. *Light oil*: is lighter than water, principally contains benzene and its homologues.

2. *Heavy oil*: sinks in water and consists principally of phenols and volatile bases and naphthaline.

3. Solid hydrocarbons.

The light oil is treated in rotation with sulphuric acid, strong potash solution, and water to remove bases and phenols, and the remaining oily portion fractionally distilled several times; the portion between 80° and 90° is then treated with about $\frac{1}{10}$ of its weight of concentrated sulphuric acid, and digested with this for some hours in order to remove hydrocarbons of the C_nH_{2n} and C_nH_{2n-2} series. It is then washed with water, and the treatment repeated if strong sulphuric acid causes any blackening when warmed with it. It is again fractionally distilled and the portion under 90° submitted to a freezing mixture, when the benzene crystallises. The crystals are pressed at a low temperature to remove liquid homologues and the crystallisation repeated several times.

At the ordinary temperature benzene is a mobile, colourless liquid, of peculiar odour, quickly causing headache if breathed, of sp. gr. ·899 at 0°. It forms large fern-shaped crystals, which melt at 5·5°. It boils at 80·5° and has a vapour density of 2·675. It is scarcely soluble in water, to which, however, it imparts its odour, but is soluble in alcohol and ether in all proportions. On gently heating it dissolves in 506 times its bulk of sulphuric acid. Benzene is largely used as a solvent for caoutchouc and guttapercha, resins, fats, &c.; it also dissolves phosphorus, sulphur, iodine, and many organic bodies. It evaporates very rapidly even at a low temperature, and burns in air with a highly luminous, smoky flame. Benzene vapour passed through a red-hot tube yields diphenyl and hydrogen :

$$2C_6H_6 = C_6H_5.C_6H_5 + H_2;$$

paradiphenyl-benzene, and small quantities of other products if the benzene be slightly impure. It forms an explosive compound with potassium when heated with it to 250°.

Most oxidising agents completely oxidise benzene to carbonic anhydride and water. Chromylic chloride, CrO_2Cl_2, however, gives in acetic solution a trichlor-quinone, $C_6HCl_3O_2$. When gently heated with sulphuric acid and manganic oxide, carbonic and formic acid are produced, and very small quantities of benzoic and phthalic acids. By heating for a long time to about 300° with concentrated fuming hydric iodide containing a small quantity of free iodine, it is converted into hexane, C_6H_{14}.

ADDITION PRODUCTS OF BENZENE.

956. On exposing a mixture of benzene with bromine to sunlight, or on passing excess of chlorine gas into benzene, also in sunlight, two kinds of products are formed, addition products (§ 947, 2) and substitution products.

Of the former the compounds $C_6H_6Br_6$ and $C_6H_6Cl_6$ are the end products of the action of these two reagents. Intermediate bodies, $C_6H_6Br_2$, $C_6H_6Br_4$, &c., no doubt exist in the crude product, but have not been isolated with certainty.

The bodies $C_6H_6Br_6$ and $C_6H_6Cl_6$ are colourless crystalline solids, insoluble in water, which decompose on heating :

$$C_6H_6Br_6 = 3HBr + C_6H_3Br_3.$$

This reaction takes place with still greater ease when they are heated with alkalies (§ 471).

Benzene hexachloride, $C_6H_6Cl_6$, melts at 157°, dissolves in warm alcohol, ether, and benzene, from which it crystallises in large needles.

Benzene hexabromide, $C_6H_6Br_6$, cannot be melted without decomposition, and is much more insoluble than the chlorine compound.

By the action of a cold aqueous solution of chlorous acid on benzene for some days, a

Benzene trichlor trihydrate, $C_6H_6Cl_3(OH)_3$, is produced. It is extracted from the mixture by shaking with ether, and forms colourless plates melting at 10°, nearly insoluble in water, but dissolving in most other solvents. On warming with dilute sodic hydrate solution it passes into

Phenose, benzene hexahydrate, $C_6H_6(OH)_6$, an amorphous hygroscopic body, which gives secondary hexyl iodide, $C_6H_{13}I$, on heating to 120° with hydric iodide.

MONO-SUBSTITUTION DERIVATIVES OF BENZENE OR PHENYL COMPOUNDS.

957. *Haloid Derivatives.*—Chlorine and bromine displace hydrogen in benzene at the ordinary temperature, especially in the presence of iodine. The first products, C_6H_5Cl and C_6H_5Br, readily pass into the higher haloid bodies, from which they require to be separated by distillation. Iodo-benzene can only be obtained by the simultaneous action of iodine and iodic acid on benzene:

$$5C_6H_6 + 2I_2 + HIO_3 = 5C_6H_5I + 3H_2O.$$

The reaction requires a temperature of about 200°. All the monohaloid compounds may be easily obtained by the action of haloid phosphorus compounds on phenol:

$$C_6H_5.OH + PCl_5 = POCl_3 + HCl + C_6H_5Cl.$$

The reaction:

$$C_6H_5.OH + HCl = H_2O + C_6H_5Cl,$$

is very difficult to obtain and requires a temperature of at least 200°.

Monochlor-benzene, phenyl chloride, C_6H_5Cl, is a colourless liquid; it boils at 132°, sp. gr. 1·128 at 0°.

Monobrom-benzene, phenyl bromide, C_6H_5Br, boils at 154°, sp. gr. 1·517.

Moniod-benzene, phenyl iodide, C_6H_5I, boils at 185°, sp. gr. 1·69.

Monofluor-benzene, phenyl fluoride, C_6H_5Fl, obtained by distilling fluobenzoic acid with lime, melts at 40° and boils a little above 180°.

Oxygen Derivatives.

958. *Hydroxy-benzene, phenyl hydrate, phenol* or *carbolic acid,* $C_6H_5.OH$, occurs in heavy coal-tar oil, in castor oil (*castoreum*), and in the urine of herbivorous animals.

It is obtained from heavy tar oil by shaking with strong soda solution, in which it dissolves to form the compound $C_6H_5.ONa$. The aqueous layer is separated from the neutral oils, and the phenol precipitated by neutralising with hydric chloride. The crude product, containing cresol and other phenols, is then dried by means of calcic chloride and distilled. The fraction obtained between 180° and 190° crystallises on cooling, the crystals being separated by pressure and filtration from the portions remaining in a liquid state.

Pure phenol forms large colourless prisms, which melt at 40°, have a peculiar smoky odour and burning taste, dissolve in 15 parts of water at the ordinary temperature and in all proportions in alcohol and ether. It boils at 183° and has sp. gr. 1·08 at 0°. It acts very powerfully on the skin, completely destroying it, and acts as an energetic poison to plants and animals, germs, &c., and for this reason is largely employed as a disinfectant and antiseptic to prevent decomposition and putrefaction in organic substances. The efficacy of the meat-smoking process depends essentially on the presence of small quantities of phenol in the smoke.

An aqueous phenol solution gives a beautiful violet reaction with ferric chloride and a white precipitate of *tribrom-phenol*, $C_6H_2Br_3.OH$, even in very dilute solutions when mixed with bromine water.

959. *Phenylates.*—These bodies are the metallic derivatives of phenol; they correspond to the alkylates, and are derived from phenol by the action of basic oxides and hydrates. They are decomposed even by carbonic acid.

The alkaline phenylates are obtained by simply dissolving phenol in the alkaline hydrate solution. They are white crystalline bodies, soluble in alcohol and ether. *Sodium phenylate*, $C_6H_5.ONa$, is more soluble than the potassic compound. Baric and calcic phenylates are also crystalline soluble compounds.

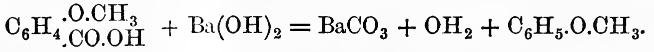
960. *Phenyl ether, oxydibenzene, diphenyl oxide*, $C_6H_5.O.C_6H_5$, is obtained by mixing diazo-benzene sulphate (§ 977) and phenol, and together with other products by the dry distillation of cupric benzoate. It crystallises in long colourless needles, melting at 28° and boiling at 246°, and is soluble in alcohol and ether, but not in water.

By heating potassic phenylate with alkyl iodides, the alkyl phenyl ethers are formed:

$$C_6H_5.O.K + IC_nH_{2+1} = KI + C_6H_5.O.C_nH_{2n+1}.$$

They are all colourless liquids, insoluble in water, and which may be distilled. On heating with strong hydric iodide to 130° they are reconverted into alkyl iodide and phenol.

Methyl-phenyl-ether, anisol, $CH_3.O.C_6H_5$, is prepared by distilling anisic acid with baric hydrate:



$$C_6H_4\begin{matrix}.O.CH_3\\.CO.OH\end{matrix} + Ba(OH)_2 = BaCO_3 + OH_2 + C_6H_5.O.CH_3.$$

It boils at 152°.

Ethyl-phenyl-ether, $C_6H_5.O.C_2H_5$, boils at 172°. *Isoamyl-phenyl-ether*, $C_5H_{11}.O.C_6H_5$, boils at 225°.

Ethylene-diphenyl-ether, $C_2H_4(O.C_6H_5)_2$, obtained from ethylene dibromide and sodium phenylate, melts at 95°.

961. *Ethereal Salts of Phenol.*—Acids do not yield salts with phenol directly, but salts may be obtained from the anhydrides and acid chlorides.

Phenyl phosphates, $C_6H_5.H_2PO_4$ and $(C_6H_5)_2HPO_4$, are prepared from phosphoric anhydride and phenol. $(C_6H_5)_3PO_4$ is obtained by the action of phosphoric chloride on phenol. Acetylic chloride acting on phenol gives *phenylic acetate*, $C_6H_5.O.CO.CH_3$, a colourless liquid boiling at 193°. Carbonic oxychloride gives a *phenylic carbonate*, $(C_6H_5O)_2CO$, forming shining colourless needles, melting at 78°.

Sulphur Derivatives.

962. *Hydro-thiobenzene, phenyl mercaptan*, $C_6H_5.SH$, prepared by the action of phosphoric sulphide on phenol, and by the reduction of phenyl sulpho-chloride with zinc and hydric chloride:

$$C_6H_5.SO_2Cl + 3H_2 = 2OH_2 + HCl + C_6H_5.SH,$$

is a colourless stinking oil of sp. gr. 1·078 and boiling point 166°–168°. With sodium it forms $C_6H_5.SNa$, and gives a mercury compound by heating its alcoholic solution with mercuric oxide:

$$(C_6H_5.S)_2Hg,$$

which on heating gives HgS and

Diphenyl sulphide, $C_6H_5.S.C_6H_5$, a colourless, disagreeably smelling oil of boiling point 292°. It is also formed during the preparation of phenyl mercaptan.

Diphenyl disulphide, $C_6H_5.S_2.C_6H_5$, is obtained by the decomposition of sodium thio-phenylate with iodine (§ 242), and from the mercaptan by oxidation with dilute nitric acid, or with atmospheric oxygen in ammoniacal solution:

$$2C_6H_5.SH + O = OH_2 + (C_6H_5.S)_2.$$

It forms colourless crystals melting at 62°, soluble in alcohol and ether.

963. *Phenyl-sulphonic acid, benzene monosulphonic acid:*

$$C_6H_5.SO_2.OH,$$

is produced by the oxidation of phenyl mercaptan or phenyl sulphide with dilute nitric acid, and by the solution of benzene in weak fuming sulphuric acid. In the latter case it is separated from the excess of sulphuric acid by dilution with water and saturation of the solution with baric or plumbic carbonates.

Baric phenyl-sulphonate, $(C_6H_5.SO_2.O)_2Ba,OH_2$, forms pearly crystals, whose aqueous solution, on exact neutralisation with sulphuric acid, gives the free sulphonic acid, which may be obtained on evaporation in four-sided tables of the formula $(C_6H_5.SO_2.OH)_2,3OH_2$.

The potassic salt of this acid, when fused with potash, gives potassic phenylate:

$$C_6H_5.SO_2.OK + 2KOH = K_2SO_3 + OH_2 + C_6H_5.OK,$$

affording a means by which benzene can be directly converted into phenol.

On warming an intimate mixture of the sodium salt of the acid with phosphoric chloride and subsequent treatment with water

Phenyl sulpho-chloride, $C_6H_5.SO_2Cl$, is produced as a colourless, heavy oil; it is crystalline below 0° and boils at 246°–247°.

It is slowly decomposed by boiling with water into phenyl sulphonic and hydrochloric acids, and is converted by tin and hydrochloric acid into phenyl mercaptan, and by ammonia into *phenyl sulphonamide*, $C_6H_5.SO_2.NH_2$. This latter forms colourless plates melting at 149°.

Phenyl sulpho-chloride, when treated with sodium amalgam in ethereal solution, gives sodic chloride and the sodium salt of *phenyl sulphinic acid:*

$$C_6H_5.SO_2Cl + Na_2 + NaCl + C_6H_5.SO_2Na,$$

from which the free acid, $C_6H_5.SO_2H$, can be obtained in large prisms, difficultly soluble in cold water and melting at 68°–69°. It is easily oxidised to the sulphonic acid, and is converted into phenyl sulpho-chloride by chlorine.

Sulpho-benzide, diphenyl-sulphuryl, $(C_6H_5)_2SO_2$, is formed by the action of sulphuric anhydride on benzene:

$$2C_6H_6 + 2SO_3 = (C_6H_5)_2SO_2 + H_2SO_4,$$

and by oxidation of diphenyl sulphide with chromic acid. It crystallises from alcohol in colourless rhombic tables, almost insoluble in boiling water, melting at 128°, and distilling without change.

Nitrogen Derivatives.

964. *Nitro-benzene*, $C_6H_5.NO_2$, is made by gradually adding benzene to cold fuming nitric acid so long as it dissolves:

$$C_6H_6 + HO.NO_2 = OH_2 + C_6H_5.NO_2,$$

and then precipitating with water. The oily product is washed with soda solution and distilled. When pure it is a light yellow oil, which may be obtained in crystals at a low temperature, and then melts at 3°; it boils unchanged at 205°; its sp. gr. = 1·2 at 0°. It is used in perfumery under the name of essence of mirbane, and is manufactured in enormous quantities for the preparation of aniline and its derivatives.

Aniline.

965. *Amido-benzene, phenylamine, aniline*, $C_6H_5.NH_2$, is found in the higher distillates from coal-tar oil, from which it may be removed along with other bases by shaking with diluted sulphuric acid. Aniline may be obtained by a variety of methods, some of which will be described in full further on.

The phenylamine or aniline used for the production of the so-called aniline colours is obtained by the reduction of crude nitro-benzene with nascent hydrogen:

$$C_6H_5.NO_2 + 3H_2 + 2OH_2 + C_6H_5.NH_2.$$

This takes place very easily in an acid solution—hydrochloric or sulphuric acid, &c., with tin or zinc, or iron and acetic acid—or in alkaline solution with arsenious oxide and grape sugar. The most general method is with iron and acetic acid—1 part of nitro-benzene, 1 part of concentrated acetic acid, and 1·2 part of iron filings or turnings. The product is finally distilled over quick-lime.

Aniline is a liquid of faint and peculiar odour, of sp. gr. 1·036 at 0°. When perfectly pure it may be crystallised on strongly cooling, and then melts at −8°. It boils at 184°, dissolves in 31 parts of water and in all proportions in alcohol and ether. Its aqueous solution gives a purple violet reaction with bleaching powder solution. With chromic acid it produces a red colour passing into blue. These reactions, which are probably due to salts of phenylene hydrazo-amido-benzene (§ 987), are used for the detection of aniline.

Aniline dissolves potassium with liberation of hydrogen and forms mono-potassium aniline, $(C_6H_5)NHK$, and probably dipotassium aniline, $(C_6H_5)NK_2$.

Aniline salts, when warmed with an equivalent quantity of argentic nitrite, are reduced to phenol with liberation of nitrogen:

$$C_6H_5.NH_2HCl + NOOAg = AgCl + OH_2 + N_2 + C_6H_5.OH$$

(comp. diazo-benzene, § 976).

966. Chemically aniline behaves very similarly to ammonia, combining with acids to form salts soluble in water and alcohol, and in many cases isomorphous with ammonic salts.

Aniline hydrochloride, $N(C_6H_5)H_3Cl$, forms colourless needles, which can be sublimed. It combines with platinic chloride to a difficultly soluble salt, $[N(C_6H_5)H_3]_2PtCl_6$.

Aniline nitrate, $N(C_6H_5)H_3O.NO_2$, crystallises in rhombic tables and prisms.

The acetate does not crystallise. The oxalate, $(N.C_6H_5.H_3)_2C_2O_4$, forms shining prisms.

The aniline compounds with the chlorides of mercury, tin, antimony, &c., correspond to the ammonia compounds.

967. Alkyl haloids combine with aniline even in the cold to form haloid salts of a phenyl-alkyl-ammonium:

$$N(C_6H_5)H_2 + C_nH_{2n+1}.I = N(C_6H_5)(C_nH_{2n+1})H_2I,$$

from which aqueous alkalies liberate phenyl-alkylamines; and on repeating the operation on these bodies *dialkyl-phenylamines* are produced, from which again *trialkyl-phenyl-ammonium iodides* can be obtained. These treated with argentic hydrate give the soluble and strongly alkaline *trialkyl-phenylammonic hydrates*, $N(C_6H_5)(C_nH_{2n+1})_3OH$.

Methyl-aniline, methyl-phenylamine, $N(C_6H_5)CH_3H$, boils at 192°.

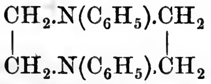
Dimethyl-aniline, $N(C_6H_5)(CH_3)_2$, boils at 192°; sp. gr. ·955. It is also obtained by heating aniline hydrochlorate with methyl alcohol to 250°.

Ethyl-aniline, $N(C_6H_5)C_2H_5.H$, boils at 204°. Sp. gr. ·954.

Diethyl-aniline, $NC_6H_5(C_2H_5)_2$, boils at 213°. Sp. gr. ·939.

Ethyl-isoamyl-aniline, $N(C_6H_5)(C_2H_5)(C_5H_{11})$, boils at 262°.

Ethylene-diphenyl-diamine, $C_2H_4(N(C_6H_5)H)_2$ (m.p. 59°), is formed by the action of excess of aniline on ethylene dibromide. When an excess of ethylene dibromide is employed, polyethylene phenyl nitrile bases result, the principal one being:



$$\begin{array}{c} CH_2.N(C_6H_5).CH_2 \\ | \qquad\qquad | \\ CH_2.N(C_6H_5).CH_2 \end{array}$$

diethylene-diphenyl-diamine, melting at 157°.

968. *Diphenylamine*, $N(C_6H_5)_2H$, obtained according to the equation:

$$N(C_6H_5)H_3Cl + N(C_6H_5)H_2 = NH_4Cl + N(C_6H_5)_2H,$$

forms colourless crystals melting at 54°, distilling undecomposed at 310°. Its salts are decomposed by water.

Triphenylamine, $N(C_6H_5)_3$, is obtained, together with the previous body, by heating potassium aniline with phenyl bromide. It melts at 127°, crystallises in tables and pyramids, and distils above 300°; is very insoluble in most menstrua, and does not form salts.

969. *Anilides.*—This term has been given to aniline derivatives in which amidic hydrogen is removed or replaced by acid or negative radicals. A great number of these bodies are known, including compounds of all possible acid groups. As they correspond in their methods of formation and chemical characters with the alkyl amides of the acid radicals (§ 636, &c.), a few only need be treated of in this place.

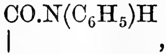
Formanilide, $N(C_6H_5)(CHO)H$, is obtained by double decomposition between ethers of formic acid and aniline, and by rapidly heating equal molecules of aniline and oxalic acid:

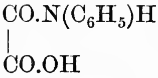
$$HO.CO.CO.OH + N(C_6H_5)H_2 = CO_2 + OH_2 + HCO.N(C_6H_5)H.$$

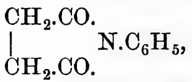
It forms colourless needles, melting at 46° and largely soluble in alcohol and water. The aqueous solution gives a precipitate of *sodium formanilide*, $HCO.N(C_6H_5)Na$, on addition of strong soda solution. It is decomposed by water alone, and by boiling with it is converted into sodic formate and aniline.

Acetanilide, $N(C_6H_5)(C_2H_5O)H$, is prepared from acetic anhydride and aniline, or by heating aniline acetate when water is split off.

It crystallises in shining leaves, melting at 112° and distilling unchanged at 295°. It is also soluble in water, alcohol, and ether, and is saponified by alkaline solutions, yielding aniline and salts of acetic acid.

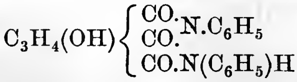
Oxanilide,  $\begin{array}{l} CO.N(C_6H_5)H \\ | \\ CO.N(C_6H_5)H \end{array}$, is obtained by heating aniline oxalate to 160°–180°. It forms shining leafy crystals, of melting point 245°, which sublime above 300°. It does not dissolve in water and ether, and only with difficulty in alcohol.

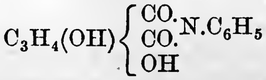
Acid aniline oxalate heated to the same temperature gives *oxanilic acid*, phenyl oxamic acid,  $\begin{array}{l} CO.N(C_6H_5)H \\ | \\ CO.OH \end{array}$, which dissolves in water and crystallises in strongly acid scales. It decomposes on heating, yielding formanilide and carbonic acid.

Phenyl succinimide,  $\left.\begin{array}{l} CH_2.CO. \\ | \\ CH_2.CO. \end{array}\right. N.C_6H_5$, is obtained as a final product when acid aniline succinate is distilled (§ 837). It forms needles melting at 155°.

Citric acid heated with aniline gives *citranilide*:

$$C_3H_4(OH)[CO.N(C_6H_5)H]_3;$$

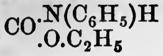
citrobianil,  $C_3H_4(OH)\left\{\begin{array}{l} \left.\begin{array}{l} CO. \\ CO. \end{array}\right. N.C_6H_5 \\ CO.N(C_6H_5)H \end{array}\right.$; and *citranilic acid:*



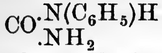
$$C_3H_4(OH)\left\{\begin{array}{l} \left.\begin{array}{l} CO. \\ CO. \end{array}\right. N.C_6H_5 \\ OH \end{array}\right.$$

the latter body being formed at a temperature of 140°.

970. *Carbanilides.*—Ethylic chloro-carbonates react energetically with aniline, forming *ethylic phenyl carbamate, phenyl urethane:*



$$\mathrm{CO}\begin{matrix}.\mathrm{N(C_6H_5)H}\\ .\mathrm{O.C_2H_5}\end{matrix}$$

and hydrochloric acid. The compound forms colourless needles of melting point 52°, which boil at 238°. On distilling with phosphoric anhydride the ethyl group is split off, and *phenylic pseudo-cyanate, carboxyl phenylamide*, $\mathrm{CO:N.C_6H_5}$, is produced as a colourless liquid boiling at 163°, which combines directly with ammonia to form *phenyl urea*,  $\mathrm{CO}\begin{matrix}.\mathrm{N(C_6H_5)H}\\ .\mathrm{NH_2}\end{matrix}$

The same body also results from the double decomposition between aniline sulphate and potassic pseudo-cyanate (§ 282), and by the continued action of cyanic acid vapour on aniline. It forms colourless needles, difficultly soluble in cold water and decomposing on heating into cyanic acid, ammonia, and diphenyl urea.

Diphenyl urea, carbanilide, $\mathrm{CO(NC_6H_5H)_2}$, is prepared by the decomposition of carboxyl diphenylimide by water (§ 282), by direct combination with aniline:

$$\mathrm{CO:N.C_6H_5 + N(C_6H_5)H_2 = CO:(NC_6H_5H)_2},$$

by heating 1 part urea with 3 parts aniline, and together with formanilide by heating oxanilide at a high temperature. It forms silky needles insoluble in water, but dissolving in alcohol and ether, melting at 205°, and volatilising unchanged.

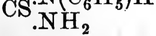
971. *Thio-carbanilides.*—On warming aniline and carbonic sulphide together, hydric sulphide is evolved and the mass solidifies to crystals of *diphenyl sulphurea:*

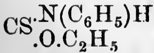
$$\mathrm{CS_2 + 2N(C_6H_5)H_2 = 8H_2 + CSN(C_6H_5.H)_2}.$$

This reaction takes place very quickly on heating equal molecules of aniline and potassic hydrate in alcoholic solution with excess of carbonic sulphide. After acidifying and evaporating the alcoholic filtrate the *sulpho-carbanilide* crystallises out in colourless plates, melting at 145° and dissolving in alcohol and ether.

Phenyl isosulphocyanate, $\mathrm{CS:N.C_6H_5}$, is obtained from diphenyl sulphurea by distilling with phosphoric anhydride, by boiling with hydrochloric acid:

$$\mathrm{CS[N(C_6H_5)H]_2 + HCl = N(C_6H_5)H_3Cl + CS:N.C_6H_5},$$

or by the action of alcoholic iodine solution, as a colourless oil of similar odour to the alkyl isosulpho-cyanates. It boils at 222° and combines again with aniline or with ammonia, in the latter case giving *phenyl sulphurea*,  $\mathrm{CS}\begin{matrix}.\mathrm{N(C_6H_5)H}\\ .\mathrm{NH_2}\end{matrix}$

It combines with alcohol at 110°, giving *phenyl xanthogenamide*,  $\mathrm{CS}\begin{matrix}.\mathrm{N(C_6H_5)H}\\ .\mathrm{O.C_2H_5}\end{matrix}$, which forms crystals melting at 65°.

972. *Phenyl Cyanamides.*—By passing dry gaseous cyanogen chloride into an ethereal solution of aniline, *cyananilide*,  $\mathrm{C}\begin{matrix}:\mathrm{N.C_6H_5}\\ :\mathrm{NH}\end{matrix}$, is produced. It may be obtained on evaporation of the ethereal solution in colourless concentrically grouped needles, difficultly soluble in water and melting at 36°-37°. An alcoholic solution of phenyl sulphurea gives the same body on heating with plumbic oxide.

It polymerises at ordinary temperatures to *triphenyl melamine*, $C_3N_3(NC_6H_5N)_3$, forming prismatic crystals melting at 162°.

Diphenyl cyanamide, $N \vdots C.N : (C_6H_5)_2$, is obtained by the action of diphenylamine and cyanogen chloride at 250°. It crystallises from ligroine or coal-tar naphtha in brilliant rhombic crystals, melting at 292°. This is in all probability a polymer of the former body = *hexaphenyl melamine*, $C_3N_3[N(C_6H_5)_2]_3$. It yields *diphenylamine* as one of its decomposition products when heated with concentrated hydric chloride.

Carbo-diphenylimide, $C(N.C_6H_5)_2$, results from the action of mercuric oxide on a boiling solution of diphenyl sulphurea in benzene:

$$CS(NC_6H_5H)_2 + HgO = HgS + OH_2 + C(N.C_6H_5)_2.$$

On evaporating the filtered solution carbo-diphenylamide remains as a syrup which gradually crystallises and polymerises, and then fuses between 168° and 170°.

A solution of carbo-diphenylimide in benzene gives, on saturation with hydric chloride, a brilliant white precipitate of

$$C(N.C_6H_5).N(C_6H_5)HCl,$$

which is decomposed on boiling with water into carbonic acid and aniline hydrochloride.

Carbo-diphenylimide combines with water to form diphenyl urea, with hydric sulphide forming diphenyl sulphurea, with ammonia and amines to form guanidine derivatives, and with carbonic sulphide at 150° to form phenyl isosulpho-cyanate.

973. *Phenyl guanidines* may be obtained from the above-mentioned bodies in many ways.

Diphenyl guanidine, $C\begin{array}{l}:NH\\:(NC_6H_5H)_2\end{array}$, is formed from diphenyl sulphurea by desulphurisation with plumbic oxide in ammoniacal alcoholic solution, by heating aniline with cyanic chloride:

$$Cl.CN + 2N(C_6H_5)H_2 = C\begin{array}{l}:NH\\:(N.C_6H_5.H)_2\end{array}$$

and by the direct combination of ammonia with carbo-diphenylimide. It crystallises in flattened needles, melting at 147°, and gives salts with one equivalent of acid, e.g. $C_{13}H_{13}N_3HCl$.

Triphenyl guanidine, $C_{19}H_{17}N_3 = C\begin{array}{l}:N.C_6H_5\\:(N.C_6H_5.H)_2\end{array}$, can also be prepared in many ways, e.g. by heating diphenyl urea or diphenyl sulphurea:

$$2CO(NC_6H_5H)_2 = OH_2 + CO:N.C_6H_5 + CN_3(C_6H_5)_3H_2,$$
$$2CS(N.C_6H_5H)_2 = H_2S + CS:N.C_6H_5 + CN_3.(C_6H_5)_3H_2;$$

by desulphurising diphenyl sulphurea in the presence of aniline:

$$CS(NC_6H_5H)_2 + NC_6H_5H_2 + HgO = HgS + OH_2 + CN_3(C_6H_5)_3H_2;$$

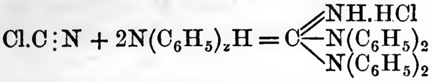
and by direct combination of carbo-diphenylimide with aniline, &c.

It is almost insoluble in water, separates from alcohol in shining rhombic prisms, m.p. 143°. It combines with one equivalent of acids to form salts. The hydrochloride has the formula:

$$C_{19}H_{17}N_3.HCl + OH_2.$$

By dry distillation it splits up into aniline and carbo-diphenylimide.

Tetraphenyl guanidine, $C_{25}H_{21}N_3$, is obtained as hydrochlorate when cyanogen chloride acts upon diphenylamine at 100°:



$$Cl.C\vdots N + 2N(C_6H_5)_2H = C\begin{array}{l}\diagup NH.HCl\\ -N(C_6H_5)_2\\ \diagdown N(C_6H_5)_2\end{array}$$

The free base crystallises from ligroine in large rhombic crystals, and on heating with alkalies splits up into ammonia and diphenylamine.

974. The following bodies also belong to the carbanilide group and may be shortly mentioned.

Carbon dichlor phenylamide, isocyan-phenyl chloride:

$$CCl_2{:}N.C_6H_5,$$

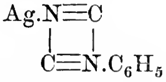
forms, together with sulphur chloride, the principal product of the action of chlorine on phenyl isosulpho-cyanate:

$$CS{:}N.C_6H_5 + 2Cl_2 = SCl_2 + CCl_2{:}N.C_6H_5.$$

It is a liquid of pungent odour, which acts powerfully on the mucous membranes, boils between 211° and 212°, and is reduced by hydric sulphide to hydrochloric acid and phenylic isosulpho-cyanate. On heating with glacial acetic acid it passes into carbon oxychloride and acetanilide:

$$CCl_2{:}N.C_6H_5 + CH_3.CO.OH = COCl_2 + NC_6H_5(C_2H_3O)H.$$

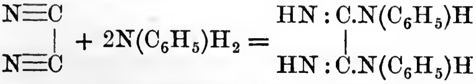
Phenyl isocyanide, phenyl carbammonium, $C\vdots N.C_6H_5$ (§ 278), is easily formed on heating chloroform, aniline, and alcoholic potash. It is a liquid of most nauseous odour, which cannot be distilled unchanged, and is decomposed by aqueous and mineral acids into aniline salts and formic acid. With metallic cyanides it combines to form crystalline compounds, e g.:



$$\begin{array}{l}Ag.N\equiv C\\ \;\;\;\;\;\;|\;\;\;\;\;|\\ \;\;\;\;C\equiv N.C_6H_5\end{array}$$

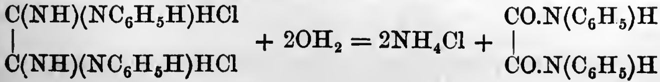
Heated to 200° for a few hours, it changes into the isomeric body benzonitrile, $N\vdots C.C_6H_5$.

Cyananiline, $C_{14}H_{14}N_4$, is prepared by leading cyanogen gas into an alcoholic aniline solution:



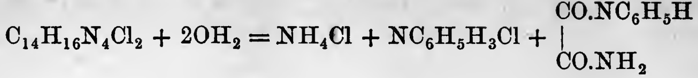
$$\begin{array}{c}N\equiv C\\ |\\ N\equiv C\end{array} + 2N(C_6H_5)H_2 = \begin{array}{c}HN{:}C.N(C_6H_5)H\\ |\\ HN{:}C.N(C_6H_5)H\end{array}$$

It crystallises in colourless plates almost insoluble in alcohol and water. It combines with two equivalents of acid to form salts, which on being boiled with water yield oxanilide:



$$\begin{array}{l}C(NH)(NC_6H_5H)HCl\\ |\\ C(NH)(NC_6H_5H)HCl\end{array} + 2OH_2 = 2NH_4Cl + \begin{array}{l}CO.N(C_6H_5)H\\ |\\ CO.N(C_6H_5)H\end{array}$$

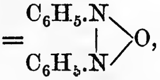
together with monophenyl oxamide:



$$C_{14}H_{16}N_4Cl_2 + 2OH_2 = NH_4Cl + NC_6H_5H_3Cl + \begin{matrix}CO.NC_6H_5H \\ | \\ CO.NH_2\end{matrix}$$

Azo-benzenes.

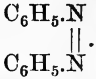
975. By the action of sodium amalgam on an alcoholic solution of nitro-benzene which is maintained slightly acid with acetic acid a reduction of the nitro-group takes place, the nitrogen atoms uniting together and so yielding azo-benzene and azoxy-benzene. Similar products are obtained on treating the alcoholic solution with strong potash, in which case some of the alcohol is oxidised to acetic acid. Azo compounds are intermediate reduction products between nitro-benzene and aniline.



Azoxy-benzene, $C_{12}H_{10}N_2O = \begin{matrix}C_6H_5.N \\ | \\ C_6H_5.N\end{matrix}\!\!>O$, results according to the equation:

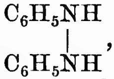
$$2C_6H_5.NO_2 + 6H = 3H_2O + C_{12}H_{10}N_2O.$$

It crystallises in long yellow needles, insoluble in water, but easily in alcohol and ether, and melting at 36°.

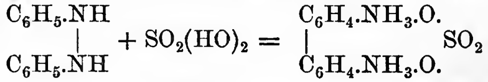


It is converted by nascent hydrogen into *azo-benzene*, $\begin{matrix}C_6H_5.N \\ \| \\ C_6H_5.N\end{matrix}$. This is best obtained by distillation of a mixture of equal parts nitro-benzene and potassic hydrate in alcoholic solution. The final distillate is a red oil, which soon crystallises. It may be obtained pure by re-crystallising from alcohol or ether, and then forms garnet red plates or tables, very much like potassic bichromate. It melts at 66°, distils unchanged at 293°, and is insoluble in water.

Azo-benzene may be also obtained by oxidation of aniline by potassic permanganate.



Nascent hydrogen from almost any source converts azo-benzene into *Hydrazo-benzene*, $\begin{matrix}C_6H_5NH \\ | \\ C_6H_5NH\end{matrix}$, which crystallises in colourless tabular crystals, melting at 131°. Oxidation converts it into azo-benzene; by distillation it splits up into aniline and azo-benzene, and in contact with strong mineral acids it yields salts of its isomer, benzidine:



$$\begin{matrix}C_6H_5.NH \\ | \\ C_6H_5.NH\end{matrix} + SO_2(HO)_2 = \begin{matrix}C_6H_4.NH_3.O. \\ | \\ C_6H_4.NH_3.O.\end{matrix}SO_2$$

Diazo Compounds.

976. Aniline salts are reduced by the action of nitrous acid into salts of diazo-benzene:

$$C_6H_5.NH_3.O.NO_2 + NO.OH = 2OH_2 + C_6H_5.N(N)O.NO_2.$$

These are very unstable bodies, which explode very readily on heating or percussion. On warming with water they decompose into nitrogen, free acid, and phenol:

$$C_6H_5.N(N).O.NO_2 + OH_2 = N_2 + HNO_3 + C_6H_5.OH.$$

By boiling with absolute alcohol benzene and aldehyde are formed:

$$C_6H_5.N_2:O.SO_2.OH + C_2H_5.OH = N_2 + C_6H_6 + SO_2(HO)_2 + C_2H_4O.$$

With the haloid acids phenyl haloid compounds are formed:

$$C_6H_5.N_2.O.NO_2 + HI = N_2 + NO_2HO + C_6H_5I.$$

977. *Diazo-benzene nitrate*, $C_6H_5.N_2.O.NO_2$, is obtained by the action of nitrous anhydride on aniline nitrate mixed with a small amount of water. The gas should be passed into the solution until potassic hydrate ceases to produce a precipitate of aniline in it. The salt may then be thrown down by the addition of alcohol in colourless needles which are insoluble in ether and benzene.

Diazo-benzene sulphate, $C_6H_5.N_2.O.SO_2.OH$, may be prepared in a similar manner to the nitrate, and also crystallises in colourless prisms.

The aqueous HCl solution of both salts yields with platinic chloride *diazo-benzene-platino-chloride*, $(C_6H_5.(N)_2Cl)_2PtCl_4$, crystallising in yellow prisms, which by distillation with potassic hydrate solution give monochlor-benzene. When heated alone it explodes somewhat violently.

Diazo-benzene nitrate, when treated with hydric bromide containing bromine, precipitates *diazo-benzene tribromide*, $C_6H_5N_2O_3$, forming large yellow plates insoluble in water and ether, difficultly soluble in alcohol.

Diazo-benzene salts, when treated with concentrated potash solution, form a potassium compound, $C_6H_5.N_2.OK$, which may be obtained pure by crystallisation from alcohol, when it forms colourless pearly prisms, which are highly explosive and are insoluble in ether. The fresh aqueous solution gives a precipitate with argentic nitrate of $C_6H_5.N_2.O.Ag$; with acetic acid a yellow aromatic oil, probably *diazobenzene hydrate*, $C_6H_5.N_2.OH$. It soon decomposes into nitrogen and phenol.

978. *Diazo-amido-benzene*, $C_6H_5N_2.NH.C_6H_5$, is obtained by passing N_2O_3 into a cold alcoholic solution of aniline:

$$C_6H_5.NH_2 + N_2O_3 = 3H_2O + C_6H_5.N_2.NH.C_6H_5;$$

also by mixing aqueous solutions of diazo-benzene salts with aniline:

$$C_6H_5.N_2.O.NO_2 + 2N(C_6H_5)H_2 = N.(C_6H_5)H_3.O.NO_2 + C_6H_5.N_2.NH.C_6H_5.$$

It separates in golden yellow needles, insoluble in water and difficultly so in cold alcohol, melting at 91° and decomposing with slight explosion at a higher temperature.

It is split up by strong hydrochloric acid into aniline hydrochloride, nitrogen, and phenol.

Metadiamido-azobenzene:

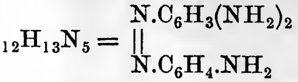
$$C_{12}H_{12}N_4 = C_6H_5-N=N-C_6H_3(NH_2)_2$$

(1 : 2 : 4), is prepared by the action of metadiamido-benzene on diazo-amido-benzene, or by the action of metadiamido-benzene and azobenzene hydrochloride:

$$C_6H_4(NH_2)_2 + C_6H_5 - N=N - Cl = C_6H_5 - N=N - C_6H_3(NH_2)_2 + HCl.$$

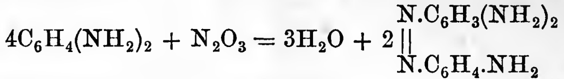
It forms slender yellow needles, sparingly soluble in water, readily in alcohol and ether; it melts at 117·5°. It is used as a yellow dye under the name of chrysoïdine.

Triamido-azobenzene, Bismarck brown:



$$C_{12}H_{13}N_5 = \begin{array}{l} N.C_6H_3(NH_2)_2 \\ \| \\ N.C_6H_4.NH_2 \end{array}$$

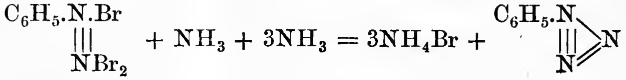
is formed by the action of nitrous anhydride on metadiamido-benzene:



$$4C_6H_4(NH_2)_2 + N_2O_3 = 3H_2O + 2\begin{array}{l} N.C_6H_3(NH_2)_2 \\ \| \\ N.C_6H_4.NH_2 \end{array}$$

It is extensively used as a brown dye.

Diazo-benzene amide, $C_6H_5N_3$, is formed by the action of diazobenzene tribromide on aqueous ammonia:



$$\begin{array}{l} C_6H_5.N.Br \\ \quad ||| \\ \quad NBr_2 \end{array} + NH_3 + 3NH_3 = 3NH_4Br + \begin{array}{l} C_6H_5.N \\ \quad\ ||| \rangle N \\ \quad\ N \end{array}$$

It is a yellowish oil, which can be distilled with steam, but explodes when heated alone. Nascent hydrogen converts it into aniline and ammonia:

$$C_6H_5N_3 + 8H = 2NH_3 + C_6H_5.NH_2.$$

Aromatic Hydrazines.

978*a*. The hydrazine compounds of the aromatic series may be obtained from the more stable diazo-benzene compounds by the action of sulphurous acid or sulphites, or by the reduction of diazo-amido-aromatic compounds by means of zinc dust and acetic acid.

A somewhat numerous series of both primary and secondary hydrazines (§ 275*a*) have in this way been obtained.

Primary Hydrazines.

978*b*. *Phenylhydrazine*, $C_6H_5.NH—NH_2$, results from the reduction of potassic diazo-benzene sulphonate with sulphurous acid.

The ordinary salts of diazo-benzene are not suitable for this reaction on account of their instability.

The following is a good method of preparation:—20 parts of aniline is dissolved in 50 parts of strong hydrochloric acid solution, to which the calculated amount of sodic nitrate in solution is added, whereby it is converted into diazo-benzene chloride; to this there is added, with continuous stirring, an excess of a very well cooled solution of sodic sulphite, and the precipitated salt of the diazo-sulphonic acid dissolved by gently warming and carefully neutralised with hydrochloric acid. The sulphurous anhydride evolved reduces most of the diazo-salt to the salt of phenylhydrazine-sulphonic acid, the reduction being completed by the addition of a little zinc dust and acetic acid. The sodic salt of phenylhydrazine-sulphonic acid separates for the most part on cooling. It is obtained in hot concentrated solution and decomposed with one-third of its volume of fuming hydrochloric acid, whereby the whole solidifies to a crystalline mass of phenylhydrazine chloride, from which the free base may be obtained, on addition of concentrated sodic hydrate, as an oily layer which may be separated, dried with potassic carbonate, and distilled. When freshly distilled it is a colourless oil of faintly aromatic odour, which solidifies in a cooling mixture to tabular crystals, melting at 23°. It boils between 233° and 234° at 750 mm. B., and is volatile in steam. Its sp. gr. = 1·091 at 21°. It is difficultly soluble in cold, somewhat easily so in hot water, and dissolves easily in most other solvents.

It is very easily oxidised, and gives a most characteristic reaction with alkaline copper solutions, the reduction to cuprous oxide taking place in the cold. The reaction serves as a test for hydrazines, and also for diazo compounds. The oxidation products in this case are nitrogen, benzene, and aniline. When HgO is used some mercury diphenyl is also produced.

Oxidising agents, haloid alkyl compounds, acid chlorides, aldehydes, cyanogen, carbonic sulphide, and oxide sulphur, &c., all act upon or form combinations with phenylhydrazine. It is a monacid base and forms mostly crystalline soluble salts. The sulphate, $(C_6H_5.N_2H_3)_2H_2SO_4$, forms white leafy crystals, insoluble in ether.

Phenyl-nitroso-hydrazine, $C_6H_5.N.(NO).NH_2$, prepared from phenylhydrazine hydrochloride and sodic nitrite, forms yellowish crystals, permanent in the air, but decomposing in closed vessels to a dark brown liquid of exceedingly pungent odour.

Monacetyl-phenylhydrazine, $C_6H_5.N_2H_2.C_2H_3O$, obtained by the action of acetic anhydride on phenylhydrazine, crystallises from hot water in fine colourless plates, melting at 128·5° and distilling almost undecomposed.

Phenyl carbazinic acid is not known in the free state, but the phenylhydrazine salt, $(C_6H_5N_2H_3)HO.CO.N_2H_2C_6H_5$, is formed by the direct combination of carbonic anhydride with the base. It is a brilliant, soft, white body, almost insoluble in water and ether.

The analogous sulphur compound, *phenylhydrazine phenyl sulphocarbazinate*, $(C_6H_5.N_2H_3)HS.CS.N_2H_2.C_6H_5$, crystallises from ether in hexagonal tables, melting at 96°.

Phenyl sulpho-carbazinic acid, $C_6H_5.N_2H_2.CS.SH$, easily decomposes either in solution in water or on warming (comp. sulphureas).

Monobenzoyl-phenylhydrazine, $C_6H_5.N_2H_2.C_7H_5O$, is formed by heating phenylhydrazine with benzoyl chloride. It melts at 168° and dissolves in hot alcohol, acetone, chloroform, and in potassic hydrate solution.

Diphenyl oxazide, $(C_6H_5.N_2H_2)_2C_2O_2$, is obtained when ethylic oxalate and phenylhydrazine are heated together. It is crystalline and melts at about 260°.

Benzylidene phenylhydrazine, $C_6H_5.N_2H.CH.C_6H_5$, is prepared from benzoic aldehyde, and the base crystallises from dilute alcohol in monoclinic crystals, melting at 152·5°.

Ethylidene phenylhydrazine, $C_6H_5—N_2H.CH.CH_3$, formed from ethyl aldehyde in a similar manner to the above, is a crystalline body which decomposes in contact with water.

Secondary Hydrazines.

978c. *Diphenylhydrazine*, $(C_6H_5)_2N—NH_2$, is metameric with hydrazo-benzene, which may be considered as a symmetrical phenyl derivative of hydrazine, $C_6H_5.HN—NH.C_6H_5$. It is obtained by the reduction of phenyl nitrosamine with zinc dust and acetic acid in well-cooled alcoholic solutions. It is an oil which does not solidify at −17°, and distils with partial decomposition into ammonia, diphenylamine, and tarry bodies. It is a monacid base, but its salts are very unstable, being partially decomposed by water.

Monobenzoyl diphenylhydrazine, $(C_6H_5)_2N_2H(CO.C_6H_5)$, crystallises from acetone in fine white shining needles, melting at 192°. It is obtained by the action of benzoyl chloride on diphenylhydrazine in ethereal solution.

Benzylidene diphenylhydrazine, $(C_6H_5)_2N_2.(CH.C_6H_5)$, prepared from benzoic aldehyde and diphenylhydrazine, may be obtained from hot alcohol in yellow crystals, melting at 122°.

Tetraphenyl-tetrazon, $(C_6H_5)_2:N_4:(C_6H_5)_2$, obtained from the action of weak oxidising agents on diphenylhydrazine in the cold, forms colourless crystals, melting at 123°, soluble in ether, alcohol, petroleum, chloroform, &c.

When ferric chloride is used as oxidising agent, nitrogen, diphenylamine, and a blue colouring matter are formed.

Phospho Derivatives.

979. When a mixture of the vapours of benzene and phosphorus trichloride is repeatedly passed through a red-hot tube,

Phosphenyl dichloride is obtained, according to the equation:

$$C_6H_6 + PCl_3 = HCl + C_6H_5.PCl_2,$$

as a colourless liquid of sp. gr. 1·319 at 20°, boiling at 222°. It refracts light strongly and fumes in the air.

It combines with chlorine to form *phosphenyl tetrachloride*, $C_6H_5.PCl_4$, a crystalline solid melting at 73°; and with bromine to form *phosphenyl dichlor-dibromide*, $C_6H_5.PCl_2Br_2$. With oxygen it forms phosphenyl oxydichloride, $C_6H_5.POCl_2$, a liquid boiling with partial decomposition at 260°.

Phosphenyl dichloride reacts with water, forming *phosphenylic acid*, $C_6H_5P(OH)_2$ or $C_6H_5.PHO.OH$, which separates from hot saturated solutions as a limpid oil, solidifying on cooling to leafy crystals. Its salts have the formula $C_6H_5PHMO_2$. With phosphorus pentachloride it gives phosphorus trichloride, phospho-oxychloride, and phosphenyl oxydichloride:

$$C_6H_5.PH_2O_2 + 2PCl_5 = PCl_3 + POCl_3 + 2HCl + C_6H_5.POCl_2.$$

The three saturated phosphenyl haloid compounds are decomposed by water into hydric haloid and the very stable dibasic

Phenyl phosphonic acid, $C_6H_5.PO(OH)_2$ (comp. § 304), which dissolves in water and alcohol and crystallises in plates melting at 158°. It decomposes at 250° into benzene and metaphosphoric acid:

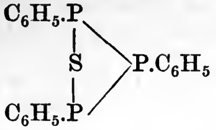
$$C_6H_5.PO(OH)_2 = C_6H_6 + PO_2OH.$$

On saturating phosphenyl dichloride with HI, a solid mass is formed, probably $(C_6H_5PI_2.HI)$, hydric chloride being expelled. It decomposes with alcohol to *phenyl phosphine*, $C_6H_5.PH_2$, a most repulsive-smelling oil, which sinks in water and boils at 160°.

Aqueous acids do not combine with it, but with hydriodic acid gas it forms *phenyl phosphonium iodide*, $PH_3.C_6H_5.I$, a solid, which reacts with water, forming phenyl phosphine and hydric iodide.

On exposure to air phenyl phosphine oxidises to *phenyl phosphine oxide*, $C_6H_5.PH_2O$, a crystalline solid easily soluble in water.

Phenyl phosphine combines with sulphur, yielding a crystalline body, melting at 138°, and possibly having the constitution:



Diphosphenyl, $C_6H_5P = P.C_6H_5$, prepared from phosphenyl chloride and phenyl-phosphine, is a yellow powder, m.p. 149°–150°, easily soluble in benzene. It probably corresponds in constitution to azobenzene.

Phenyl Mercury Compounds.

980. *Mercury diphenyl*, $C_6H_5.Hg.C_6H_5$, is easily obtained on heating brom-benzene, diluted with benzene, with sodium amalgam, a small quantity of ethylic acetate being added to the mixture in order to start the reaction. It forms rhombic crystals, becoming yellow on exposure to light, melts at 120°, and sublimes mostly unchanged, a small amount, however, being decomposed into mercury, diphenylbenzene, and carbon. It is insoluble in water and only slightly soluble in alcohol and ether; benzene dissolves it easily.

Free halogens act upon it according to the equations:

$$Hg:(C_6H_5)_2 + 2Cl_2 = 2C_6H_5Cl + HgCl_2$$

and

$$Hg(C_6H_5)_2 + Cl_2 = C_6H_5Cl + Cl.Hg.C_6H_5.$$

Haloid phenyl mercury compounds are also formed when mercury diphenyl is heated with haloid mercury salts and alcohol:

$$C_6H_5.Hg.C_6H_5 + HgI_2 = 2(C_6H_5.Hg.I).$$

They all crystallise in rhombic tables and melt at something above 250°. When heated with moist argentic oxide the halogen atom is removed, *mercury phenyl hydrate* being produced.

It is a powerful base, which crystallises in prisms and gives salts with acids.

Tin Phenyl Compounds.

980*a*. Mercury diphenyl, when heated with stannic chloride in solution in naphtha, gives stan-diphenyl dichloride:

$$SnCl_4 + 2(C_6H_5)_2Hg = 2Hg(C_6H_5)Cl + SnCl_2.(C_6H_5)_2.$$

Stan-diphenyl dichloride forms beautiful colourless triclinic crystals, melting at 42°, soluble in alcohol, and decomposing on boiling with water to *stan-phenoxychloride*, $Sn(C_6H_5)Cl.OH$, an insoluble powder melting at 187°. It yields stannic chloride and benzene on boiling with concentrated hydric chloride.

Arsen-phenyl Compounds.

980*b*. *Phenyl-arsen-chloride*, $AsCl_2C_6H_5$, obtained by heating arsenious chloride and mercury diphenyl, is a colourless liquid boiling at 252°–255°, decomposed by water with great difficulty, but easily by alkalies. A potassic compound, $C_6H_5As(OK)_2$, is soluble in alcohol. It combines directly with chlorine, forming *phenyl arsen-tetrachloride*, $C_6H_5AsCl_4$, a yellow liquid which reacts violently with water, yielding *monophenyl-arsonic acid*, $C_6H_5.AsO.(OH)_2$, white needles melting at 168°.

Diphenyl-arsen-chloride, $(C_6H_5)_2AsCl$, is an oily liquid.

Diphenyl-arsen-trichloride, $(C_6H_5)_2AsCl_3$, is a solid which decomposes with water, yielding

Diphenyl-arsonic acid, $(C_6H_5)_2AsO.(OH)$, which crystallises in fine needles, melting at 174° and easily soluble in hot water.

Phenyl-arsen-oxide, C_6H_5AsO, has an odour like anise; it is insoluble in water and melts at 119°–120°.

It gives *triphenyl-arsine*, $(C_6H_5)_3As$, on heating above its melting point.

Phenyl-arsen-oxychloride, $C_6H_5AsOCl_2$, prepared from the tetrachloride by the action of water, is solid, melts about 100°, and dissolves easily in water.

BENZENE DISUBSTITUTION PRODUCTS, PHENYLENE COMPOUNDS.

981. A very large number of disubstituted benzene compounds is known. The number of known isomers in any case amounts at most to three. Dihaloid benzenes can be prepared by the direct action of the halogen with the aid of heat. The product is generally a mixture of two isomers, of which one is solid and usually exceeds the other in amount.

The crystalline isomer may be considered to belong to the para series, as it can be converted into terephthalic acid, according to the equation :

$$C_6H_4Br_2 + 2ClCO.O.C_2H_5 + 2Na_2 = 2NaCl$$
$$+ 2NaBr + C_6H_4(CO.O.C_2H_5)_2,$$

and further yields only a single tri-derivative (comp. § 954).

In the case of the dibrom-benzenes another isomer has been converted in a similar manner into isophthalic acid, and also has been shown to yield three tribrom-benzenes on further bromination, thus proving it to be the meta derivative, so that the ortho position alone remains for the third dibrom-benzene.

In cases where different radicals are substituted—for instance, nitro-haloid benzenes, obtained by nitrating haloid benzenes—two isomers result, of which one appears to be the ortho, the other the para compound. This is also the case with the haloid and nitro products of phenol and the phenol sulphonic acids.

Halogen and Nitro Derivatives.

982. *Dichlor-benzenes*, $C_6H_4Cl_2$. All three modifications of this body are known.

Orthodichlor-benzene is obtained by the action of phosphoric chloride on ortho-chlor phenol, and by the direct chlorination of benzene; it is a liquid boiling at 179° and of sp. gr. 1·3278 at 0°.

Metadichlor-benzene is obtained from metachlor-aniline, by conversion of this latter, by treatment with nitrous acid, into diazochlor-benzene, the platinochloride of which, on distillation with sodic carbonate, yields metadichlor-benzene as a colourless oil, boiling at 170°–172°. It is also obtained by the action of phosphoric chloride on metachlor-phenol.

Paradichlor-benzene is prepared by the direct chlorination of benzene in the presence of iodine, and is separated from the other products by fractional distillation; it is also prepared by the action of phosphoric chloride on parachlor-phenol. It crystallises in monoclinic prisms, melts at 54°, and boils at 173°–174°.

Dibrom-benzenes, $C_6H_4Br_2$. *Orthodibrom-benzene* appears to be formed in small quantity by the action of bromine on benzene, but has not yet been obtained in a state of purity from that source. It can be prepared by the action of phosphoric bromide on orthobrom-phenol and hydro-quinone, or from orthobrom-aniline, which is first converted into the nitrate, then treated with nitrous acid, whereby orthobrom-diazo-benzene is formed:

$$C_6H_4Br.NH_3.O.NO_2 + NOHO = C_6H_4Br.N_2.ONO_2.$$

This is then converted into perbromide by treatment with bromine water, and the pure diazobrom-benzene perbromide distilled with sodic carbonate, when orthodibrom-benzene distils.

It crystallises at − 6°, melts at − 1°, boils at 223°–224°, and has sp. gr. 2·003 at 0°. On nitration it yields two nitro-orthodibrom-benzenes, of which the principal ($NO_2 : Br : Br = 1 : 3 : 4$) melts at 58·6°.

Metadibrom-benzene is obtained from metabrom-aniline by the 'diazo reaction' described above; it is also obtained from the dibrom-aniline prepared by direct bromination of acetanilide and distillation with potassic hydrate, by dissolving it in alcohol saturated with nitric acid; dibrom-diazo-benzene is first formed, but this reacts with the alcohol, forming nitrogen, aldehyde, and dibrom-benzene (comp. § 976).

Metadibrom-benzene can also be obtained by the action of phosphoric bromide on metabrom-phenol; it is still liquid at — 20°, boils at 219°, and has sp. gr. 1·955 at 18·6°. On treatment with nitric acid it yields two nitro-metadibrom-benzenes. One

$$(NO_2 : Br : Br = 1 : 2 : 4)$$

melts at 61·6°, the other ($Br : NO_2 : Br = 1 : 2 : 3$) melting at 82·6°. A third ($NO_2 : Br : Br = 1 : 3 : 5$) is only obtained indirectly.

Paradibrom-benzene is the chief ingredient of the mixture of dibrom-benzenes obtained by direct bromination of benzene, and is obtained on cooling in crystals; it can also be prepared by the action of phosphoric bromide on parabrom-phenol, and from parabrom-aniline by the 'diazo reaction.' It crystallises in monoclinic prisms, melts at 89°, and boils at 218·6°; on treatment with nitric acid it yields only a single nitro-paradibrom-benzene:

$$(Br : NO_2 : Br = 1 : 2 : 4),$$

melting at 85·4°.

Diiodo-benzenes can be obtained by the 'diazo reaction' from the corresponding iodo-anilines.

Ortho-diiodo-benzene is a crystalline body, boiling at a higher temperature than its isomerides; meta-iodo-benzene forms brilliant laminæ, melting at 40·5°, and boils at 285°.

Paraiodo-benzene is also obtained by the action of iodine and iodic acid on benzene; it crystallises in laminæ, melts at 129·4°, and boils at 277°.

983. *Ortho-* and *para-halogen nitro-benzenes* are obtained by the action of fuming nitric acid on the halogen benzenes; they can also be obtained, as can the meta derivatives, from the nitranilines by means of the 'diazo reaction.' The following are known:—

$C_6H_4Cl(NO_2)$, *orthochlor-nitrobenzene*, melts at 32·5° and boils at 243°.

Metachlor-nitrobenzene, is obtained by the action of chlorine on nitro-benzene mixed with iodine; it melts at 48° and boils at 233°.

Parachlor-nitrobenzene, the principal product of the action of nitric acid on monochlor-benzene, melts at 83° and boils at 242°.

$C_6H_4Br.NO_2$, *orthobrom-nitrobenzene*, forms long needles, melting at 43·1° and boiling at 261°.

Metabrom-nitrobenzene, melts at 56° and boils at 256·5°.

Parabrom-nitrobenzene, melts at 125·5° and boils at 255°.

$C_6H_4I.NO_2$, *ortho-iodonitro-benzene*, melts at 49·4°.

Metiodo-nitrobenzene, melts at 36° and boils at 280°.

Pariodo-nitrobenzene, melts at 171·4°.

984. *Dinitro-benzenes*, $C_6H_4(NO_2)_2$.—A mixture of the three dinitro-benzenes is readily obtained by slowly adding benzene to a mixture of one volume of fuming nitric acid and two volumes of sulphuric acid; it is then precipitated by addition of water and crystallised from alcohol. The product so obtained consists mainly of *metadinitro-benzene*, and can be obtained in a state of purity by several recrystallisations from hot alcohol. It then forms thin flexible needles and melts at 89·9°. The mother liquors still contain two other dinitro-benzenes, which may be separated from each other by repeated crystallisation.

Ortho-dinitrobenzene forms colourless opaque needles or striated plates, melts at 117·9°, and yields ortho-nitraniline on reduction.

Paradinitro-benzene forms colourless flat needles, melting at 172°, and is converted into paranitraniline by reducing agents.

Substituted Anilines.

985. All aniline derivatives in which one of the benzene hydrogen atoms is substituted by a negative radical still possess slightly basic characters; the diamido-benzenes are diacid bases.

Nitro-amidobenzenes, $C_6H_4(NO_2).NH_2$. *Ortho-nitraniline* is obtained by heating orthobrom-nitrobenzene with alcoholic ammonia to 180°:

$$C_6H_4Br.NO_2 + 2NH_3 = NH_4Br + C_6H_4(NO_2).NH_2.$$

It forms yellow crystals, melting at 117·9°. It is also obtained, together with the para derivative, from the result of the action of nitric acid on acetanilide.

Metanitraniline is formed by passing sulphuretted hydrogen into an ammoniacal alcoholic solution of metadinitro-benzene:

$$C_6H_4(NO_2)_2 + 3SH_2 = 2H_2O + 3S + C_6H_4(NO_2).NH_2.$$

It forms long yellow needles, melting at 109·9°.

Paranitraniline.—Nitric acid acting on acetanilide converts it into a mixture of ortho- and para-nitracetanilides. Alkalies convert this into the corresponding nitranilines, of which the para compound greatly preponderates and can be separated by crystallisation. It can also be obtained by the reduction of paradinitro-benzene. It crystallises in yellow needles or tables and melts at 145·9°.

Nitroso-dimethyl-aniline, $C_6H_4(NO)N(CH_3)_2$, is obtained as hydrochloride on treating dimethyl-aniline in hydrochloric acid solution with amylic nitrite. On distillation with soda the base is obtained in green plates, melting at 85°. It forms compounds with aniline, phenol, argentic nitrate, &c., which crystallise very beautifully. The compound $2C_6H_4(NO)N.(CH_3)_2 + C_6H_5NH_2$ forms steel blue crystals, which appear green by transmitted light. Nitric acid oxidises nitroso-dimethyl aniline to nitro-dimethyl aniline, $C_6H_4(NO_2)N(CH_3)_2$.

986. *Halogen Amido-benzenes.*—The monochlor- or brom-derivatives cannot be obtained by the action of chlorine and bromine on aniline, as this only yields the tri-products. Iodine, however, converts aniline into pariodaniline.

Monochlor-anilines, $C_6H_4Cl(NH_2)$. *Orthochlor-aniline* is obtained by the action of tin and hydrochloric acid on orthochlor-nitro-benzene. It is a liquid boiling at 207°, of sp. gr. 1·2338 at 0°. It is a much weaker base than its isomerides.

Metachlor-aniline, prepared by the reduction of metachlor-nitrobenzene, is liquid, boils at 230°, and has sp. gr. 1·2432 at 0°.

Parachlor-aniline, prepared by the reduction of parachlor-nitrobenzene, by distillation of chlorisatine with alkalies, and from chlorphenyl-acetamide, $C_6H_4Cl.N(C_2H_3O)H$, forms brilliant rhombic prisms, melts at 70°–71°, and boils at 231°.

Brom-anilines.—These compounds are prepared like the corresponding chlor-anilines. A mention of their melting and boiling points will therefore suffice.

Monobrom-anilines, $C_6H_4Br.NH_2$.

Orthobrom-aniline melts at 31°–31·5° and boils at 229°.

Metabrom-aniline melts at 18°–18·5° and boils at 251°.

Parabrom-aniline, colourless regular octahedrons, melts at 63°.

Iodo-anilines, $C_6H_4I.NH_2$. *Meta-iodaniline* is prepared by reducing meta-iodonitro-benzene. It crystallises in brilliant laminæ and melts at 25°.

Para-iodaniline is obtained by reduction of paranitroiodo-benzene and by the action of iodine on aniline. It crystallises in needles, melting at 60°.

987. *Diamido-benzenes*, or *phenylene diamines*, $C_6H_4(NH_2)_2$. *Ortho-diamido-benzene*, or *γ-phenylene diamine*, is prepared by the reduction of ortho-nitraniline, it melts at 99° and boils at 252°.

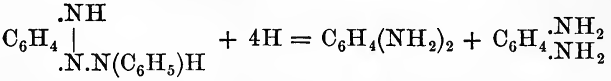
Metadiamido-benzene, or *α-phenylene diamine*, obtained by the reduction of metanitraniline, forms prisms melting at 64° and boiling at 287°.

Paradiamido-benzene, or *β-phenylene-diamine*, is obtained by the reduction of paranitraniline in scaly crystals, melting at 140° and boiling at 267°.

Nitroso-dimethyl aniline is reduced by nascent hydrogen to dimethyl diamido-benzene, $C_6H_4(NH_2)N(CH_3)_2$.

Amido-azobenzene, $C_{12}H_{11}N_3 = C_6H_5.N_2C_6H_4.NH_2$, is isomeric with diazo-benzene amido-benzene (§ 978), from which it may be formed by allowing its alcoholic solution mixed with an aniline salt to stand for a few days. The compound may be thrown down by water and recrystallised from alcohol. It then forms rhombic prisms, melting at 130° and volatilising at a higher temperature. It forms violet-coloured salts with acids, which dye silk red.

Nascent hydrogen reduces it to aniline and paraphenylene-diamine:



$$C_6H_4\begin{array}{l}.NH\\ |\\ .N.N(C_6H_5)H\end{array} + 4H = C_6H_4(NH_2)_2 + C_6H_4\begin{array}{l}.NH_2\\ .NH_2\end{array}$$

Aniline yellow consists for the most part of this substance.

987*a*. *Dicyano-benzenes*, $C_6H_4(CN)_2$. *Metadicyano-benzene*, 1 : 3, is prepared by the distillation of a mixture of potassic benzene-meta-disulphonate and potassic cyanide. It melts at 160° and yields isophthalic acid on saponification.

Paradicyano-benzene, 1 : 4, is similarly prepared from benzene paradisulphonic acid, melts at 220°, and gives terephthalic acid on saponification.

Metanitro-cyanobenzene, $C_6H_4(NO_2).CN$, is a crystalline body, obtained by the action of nitric acid on cyano-benzene.

Substituted Phenols.

988. By the action of chlorine on phenol two isomeric mono-chlor-phenols are obtained: *orthochlor-phenol*, $C_6H_4Cl.OH(1:2)$, a colourless oily liquid, boiling at 176°–177°, solidifying at − 12°, and melting at − 7°; and *parachlor-phenol*, $C_6H_4Cl.OH(1:4)$, a crystalline body, melting at 41° and boiling at 218°.

Metachlor-phenol, $C_6H_4Cl.OH(1:3)$, prepared from metachlor-aniline, is an oil boiling at 214°.

The brom-phenols, $C_6H_4Br.OH$, are produced similarly to the chlor compounds.

Orthobrom-phenol is a colourless oil.

Metabrom-phenol is an oil boiling at 227°–229°.

Parabrom-phenol forms colourless monoclinic crystals, melts at 66°, and boils at 236°.

Iodo-phenols, $C_6H_4I.OH$. As before stated, the three isomers are formed simultaneously.

The liquid isomer, and that one of the solids melting at 64°–66°, are volatile in a current of steam. The third non-volatile solid melts at 87° and is somewhat soluble in water. Both solid isomers may be obtained from the iodo-anilines by conversion into the sulphate of diazo-iodobenzene and decomposition of this by boiling water.

Though the constitution of these bodies is still uncertain, yet it is probable that the liquid is the ortho compound, the solid melting at 89° the meta, and that melting at 64°–66° the para derivative.

989. *Nitro-phenols,* $C_6H_4(NO_2).OH$. Two isomeric nitro-phenols (ortho and para) are produced by the action of dilute nitric acid on phenol.

They may be separated by distillation with steam. *Ortho-nitro-phenol* passes over and crystallises from water in sulphur yellow prisms, melting at 45° and boiling at 214°. *Paranitro-phenol* forms white prisms, melting at 114°.

Metanitro-phenol may be obtained from the metanitraniline (melting at 108°) by conversion into the diazo-benzene nitrate and decomposition of this salt by water. It forms colourless non-volatile prisms, pretty soluble in water and melting at 96°. It may also be obtained from the sulphonic acid of metadinitro-benzene, melting at 90°.

Dinitro-phenols.—Ortho-nitro-phenol under the influence of nitric acid is converted into the *dinitro-phenols,* 1 : 2 : 4 and 1 : 2 : 6.

The first forms yellowish tabular crystals, melting at 114°, and is also obtained from paranitro-phenol (m.p. 114°). The 1 : 2 : 6 compound melts at 64°.

On still further nitration these two dinitro-phenols yield an identical *trinitro-phenol* or picric acid, $C_6H_2(NO_2)_3.OH$, 1 : 2 : 4 : 6, m.p. 120°.

Metanitro-phenol gives also two modifications of dinitro-phenol, γ and δ—one melting at $104° = \gamma$, pretty soluble in hot water, easily in alcohol and ether; the other, δ, fine silky needles, melting 141° and separating in a liquid state from its solutions.

They yield an isopicric acid, on nitration, melting at 174°, easily soluble in hot water.

Nitroso-phenol, $C_6H_4(NO)OH$, is obtained along with dimethylamine by boiling nitroso-dimethyl aniline with alkalies. After acidifying with sulphuric acid it may be extracted with ether, from which it crystallises in yellow prisms, m.p. 120°–130°, moderately soluble in water. It may also be obtained by direct action of nitrous acid on phenol. Nitric acid oxidises it to paranitro-phenol, m.p. 114°. It forms a sodium compound, $C_6H_4(NO).ONa$, with sodic hydrate solution, and on reduction is converted into paramido-phenol.

Amido-phenols, $C_6H_4(NH_2)OH$, result from the reduction of nitro-phenols by tin and hydrochloric acid. They are colourless crystalline bodies, difficultly soluble in cold water and giving crystalline salts with acids. Ortho- and para-nitro-phenol yield an amido-phenol, melting at 170°. From paraortho-dinitro-phenol and trinitro-phenol or picric acid the respective diamido-phenols, $C_6H_3(NH_2)_2OH$, and triamido-phenol, $C_6H_2(NH_2)_3OH$, have been obtained.

By partial reduction the dinitro-phenols give amido-nitro-phenols, of which the following are the examples as yet known :

$$C_6H_3(NO_2)(NH_2).OH$$

from 1 : 2 : 4 dinitro-phenol, and $C_6H_2(NO_2)_2(NH_2)OH$ and

$$C_6H_2(NO_2)(NH_2)_2OH$$

from picric acid.

Alkyl nitrites act on amido-nitro-phenols, replacing the amido group by hydrogen, paranitro-phenol being at the same time produced. This seems to show that the ortho-nitro groups in nitrophenols are the first to suffer reduction to NH_2.

Sulphonic Acids.

990. *Halogen Benzene-sulphonic Acids.* — *Parachlor-benzene-sulphonic acid,* $C_6H_4Cl.SO_2.OH$, is obtained by the action of Nordhausen sulphuric acid on monochlor-benzene. The ortho and meta compounds are also known. All three varieties of the *brom-benzene-sulphonic acids,* $C_6H_4Br.SO_2.OH$, have been obtained, similarly to the chlor compounds. *Ortho-iodo-benzene-sulphonic acid:*

$$C_6H_4I.SO_2.OH,$$

is obtained by the action of Nordhausen sulphuric acid on iodobenzene.

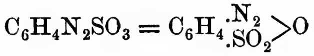
By treatment of benzene-sulphonic acid with nitric acid, or of nitro-benzene with Nordhausen sulphuric acid, the three isomeric *nitro-benzene-sulphonic acids* have been obtained, the meta compound being always formed in largest proportion. Their salts exhibit well-characterised differences, but only the meta acid, which crystallises in large deliquescent plates, has yet been obtained definitely in the free state.

The corresponding amido-benzene-sulphonic acids are prepared by reduction of the nitro-acids. *Para-amido-benzene-sulphonic acid* is also obtained by the action of sulphuric acid on aniline, and is therefore termed *sulphanilic acid*; it crystallises in large rhombic tables of the formula $C_6H_4(NH_2).SO_2.OH,H_2O$, is difficultly soluble in cold water (112 parts at 15°), readily in hot water, insoluble in alcohol and ether.

Meta-amido-benzene-sulphonic acid generally crystallises in anhydrous needles.

Orthamido-benzene-sulphonic acid generally crystallises in rhombohedrons of the formula $2C_6H_4(NH_2).SO_2.OH,H_2O$.

Ortho- and meta-amido-benzene-sulphonic acids are reduced by nitrous acid to the corresponding *diazo-acids:*



$$C_6H_4N_2SO_3 = C_6H_4\begin{matrix}.N_2\\.SO_2\end{matrix}\!\!>O$$

The *ortho* compound forms rhombic plates and gives off nitrogen on boiling with water.

The *meta* acid forms small reddish yellow prisms, which explode when heated and are decomposed by water at 60° with evolution of nitrogen.

Phenol-sulphonic acids, $C_6H_4(OH).SO_2OH$. Two isomeric acids of this formula are obtained by dissolving phenol in sulphuric acid. At ordinary temperatures *ortho-phenol-sulphonic acid* is obtained in largest quantity, which yields readily soluble salts; this acid on heating is converted into *paraphenol-sulphonic acid,* whose salts are more difficultly soluble and therefore crystallise first from a mixture of both. As a rule the potassic salts are employed for separation, the para salt crystallising in six-sided tables, $C_6H_4(OH)SO_2.OK$, whilst later the more readily soluble ortho salt separates in prisms of the formula $C_6H_4(OH)SO_2.OK,2H_2O$.

Excess of sulphuric acid or long heating must be avoided in the preparation of these acids; otherwise *phenol-disulphonic acid:*

$$C_6H_3(OH)(SO_2.OH)_2,$$

will be the principal product.

Benzene-disulphonic acids, $C_6H_4(SO_2.OH)_2$. The meta and para compounds are known, and are both obtained by the action of sulphuric acid on benzene-monosulphonic acid or of fuming sulphuric acid on benzene, the product mainly consisting of the former if the temperature be kept low, whilst the para acid predominates at higher temperatures; the acids being best separated by means of the different solubilities of their potassic salts, the para salt being least soluble.

Diphenols, $C_6H_4:(OH)_2$.

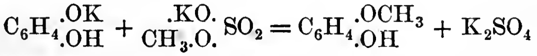
991. All the possible isomeric bodies of this formula are known, and the relative positions of the hydroxyl groups have been settled with comparative certainty.

992. *Pyrocatechin, catechol = ortho-dioxy-benzene,* may be obtained by the dry distillation of catechu, kino, and some other tanning materials, and also from the liquid ortho-haloid-phenols and from ortho-phenol-sulphonic acid by the action of fused potash. Cellulose heated with water for a long time to 200° is also said to yield ortho-dioxy-benzene. It is readily soluble in water, alcohol, and ether, and crystallises in quadratic prisms, melting at 102°. It volatilises below its melting point and boils at about 245°. Its aqueous solutions are coloured green by ferric salts, the colour being changed by alkalies to red or violet. It forms a precipitate with lead salts of $C_6H_4:O_2:Pb$, and its solutions reduce gold, silver, and platinum salts. Nitric acid oxidises it to oxalic acid.

Diacetyl pyrocatechin, $C_6H_4(OC_2H_3O)_2$, crystallises from alcohol in easily fusible needles.

A tetrabrom compound, $C_6Br_4(OH)_2$, is formed by heating protocatechuic acid to 100° with bromine, or by the direct action of the halogen on the phenol.

Methyl pyrocatechin, $C_6H_4\begin{matrix}.O.CH_3\\.OH\end{matrix}$, or *guaiacol,* is obtained by the dry distillation of guaiacol resin and from beech-wood creasote, also synthetically by heating pyrocatechin, potassic hydrate, and potassic methyl sulphate together to 180°:



$$C_6H_4\begin{matrix}.OK\\.OH\end{matrix} + \begin{matrix}.KO.\\CH_3.O.\end{matrix}SO_2 = C_6H_4\begin{matrix}.OCH_3\\.OH\end{matrix} + K_2SO_4$$

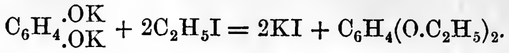
It is a colourless liquid, boiling at 200°, forming crystalline compounds with alkalies, e.g. $C_6H_4(O.CH_3)OK$, and splitting up on heating with hydriodic acid into methylic iodide and pyrocatechin.

Dimethyl pyrocatechin, $C_6H_4(O.CH_3)_2$, boils at 205°–206°.

993. *Resorcin, metadioxy-benzene,* is formed by the distillation of many resins—galbanum, assafœtida, sagapenum, &c.—with potassic hydrate. It is, however, most easily obtained by the dry distillation of extract of Brazil wood (= brazilin $C_{22}H_{18}O_7$ and umbelliferon $C_7H_6O_3$). It has also been obtained from meta- and para-bromphenol, and from benzene meta- and para-disulphonic acids, and from haloid benzene sulphonic acids by fusion with alkalies. It forms colourless triclinic tables and prisms, which are very soluble in water, melt at 110°, and boil at 271°. Ferric chloride colours its aqueous solution deep violet. Ammonia removes the colour.

The *diacetate*, $C_6H_4(OC_2H_3O)_2$, is a colourless oil.

On warming with alkalies and ethyl iodide a diethyl ether, b.p. 251°, is formed:



$$C_6H_4\begin{matrix}.OK\\.OK\end{matrix} + 2C_2H_5I = 2KI + C_6H_4(O.C_2H_5)_2.$$

Pentachlor-resorcin, $C_6HCl_5O_2$, melts at 92·5°.

Pentabrom-resorcin, $C_6HBr_5O_2$, melts at 113·5°.

Hydriodic acid reduces them to trihaloid compounds.

Mononitro-resorcin, $C_6H_3(NO_2)(OH)_2$, prepared by the action of nitrous acid on an ethereal solution of resorcin, melts at 115°, and gives by the action of bromine a dibrom-nitro-resorcin, melting at 114°.

994. *Hydro-quinone, paradioxy-benzene*, was first obtained by the dry distillation of quinic and dioxy-benzoic acids, or by oxidising quinic acid with plumbic peroxide. It is also obtained by the decomposition of its glucoside, *arbutin*, with dilute acids; by the action of nascent hydrogen or reducing agents (usually sulphurous acid or hydriodic acid in aqueous solution) on quinone, $C_6H_4O_2$; by heating diazo-phenol sulphate, obtained by the action of nitrous acid on phenol in ethereal solution, with excess of sulphuric acid; and from pariodo-phenol by fusion with potassic hydrate.

It forms colourless rhombic plates and prisms, melting at 159° and readily subliming in glistening plates. It has a sweet taste and is readily converted by oxidising agents into quinhydrone and quinone.

Haloid derivatives are produced by the reduction of haloid quinone compounds.

Monochlor-hydro-quinone, $C_6H_3Cl(OH)_2$, is soluble in water, alcohol, and ether.

Dichlor-hydro-quinone, $C_6H_2Cl_2(OH)_2$, m.p. 164°, sublimes at 120° and is almost insoluble in water.

Trichlor-hydro-quinone, $C_6H.Cl_3.(OH)_2$, forms plates, m.p. 134°, soluble in boiling water.

Tetrachlor-hydro-quinone, $C.Cl_4(OH)_2$, is insoluble in water.

The corresponding bromine compounds are known; they resemble the chlorine bodies very closely.

No iodo-hydro-quinones are known, but a dinitro compound, $C_6H_2(NO_2)_2(OH)_2$, has been obtained, forming yellow crystals.

The sulpho compounds of these phenols have not been much studied.

Arbutin, $C_{25}H_{34}O_{14}$, is a glucoside of *hydro-quinone*. It is contained in the leaves of *Arbutus uva ursi* and *Pyrola umbellata*, from which it may be obtained by treating the aqueous extract with plumbic acetate and decomposing the filtrate with hydric sulphide. The filtrate from the plumbic sulphide gives on evaporation silky needles of a bitter taste, soluble in water, difficultly so in alcohol and ether, and of m.p. 170°. It yields quinone on distillation with an oxidising agent and a chlorinated quinone on treatment with chlorine.

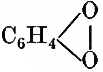
Tetranitro-arbutin, $C_{25}H_{30}(NO_2)_4O_{14}$, is said to be produced by the action of concentrated nitric acid. It gives an acetyl derivative, as does arbutin itself.

Quinone.

995. Bodies of this class are formed from aromatic hydrocarbons by the replacement of two hydrogen atoms by two oxygen atoms, which are supposed to be so linked together as to form a diad group, and as such are always combined directly to the carbon nucleus.

Quinone, $C_6H_4O_2$, results from the oxidation of hydro-quinone; by the distillation of many plant extracts with oxidising substances, most readily from quinic acid, on heating with a mixture of sulphuric acid and manganic oxide; by the oxidation of para-amido-phenol, paradiamido-benzene, benzidine, or dipara-amido-diphenyl, but best of all from aniline by oxidation with chromic mixture. It forms golden yellow prisms, melting at 116° and which volatilise at the ordinary temperature. It has a pungent odour, somewhat like iodine, and attacks the eyes violently. It acts as a kind of peroxide, converting sulphurous acid into sulphuric:

$$C_6H_4O_2 + SO(OH)_2 + OH_2 = C_6H_4(OH_2) + H_2SO_4,$$

hydro-quinone being produced, in consequence of which the constitutional formula  $C_6H_4\langle\begin{smallmatrix}O\\|\\O\end{smallmatrix}$ has been assigned to it.

Bodies which yield quinone on oxidation alone yield haloid quinones when submitted to the simultaneous action of halogens and oxidising substances. For the preparation of chlorine derivatives the ordinary mixture of manganic oxide, sodic chloride, and sulphuric acid may be used with quinic acid. In this way mono and higher chlorine products are formed.

Monochlor-quinone, $C_6H_3ClO_2$, melts at 100°.

Dichlor-quinone, $C_6H_2Cl_2O_2$, is formed along with the mono as above, and also from trichlor-phenol by powerful oxidising agents. It melts at 120°.

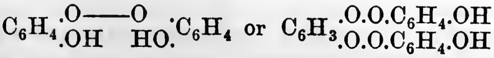
Trichlor-quinone, $C_6HCl_3.O_2$, melts at 165° and is insoluble in water.

Mono- and dibrom-quinones have not been prepared.

All the chlor-quinones yield sulphonic acids by the action of acid alkaline sulphites.

996. *Quinhydrone.*—This body is formed on mixing solutions of quinone and hydro-quinone, and also by the incomplete oxidation of hydro-quinone and by the incomplete reduction of quinone. It forms shining gold green needles.

Its formula is not yet determined with absolute certainty. It may be either



$$C_6H_4\begin{matrix}.O\text{——}O.\\ .OH \quad HO.\end{matrix}C_6H_4 \quad \text{or} \quad C_6H_3\begin{matrix}.O.O.C_6H_4.OH\\ .O.O.C_6H_4.OH\end{matrix}$$

1. *Pheno-quinone*, $C_{18}H_{14}O_4$, results when aqueous solutions of

phenol and quinone are mixed, and also by careful oxidation of phenol:

$$2C_6H_4O_2 + 2HO.C_6H_5 = C_6H_4(OH)_2 + C_6H_4(O.O.C_6H_5)_2.$$

This seems to be a general reaction with phenols.

Pheno-quinone forms red needles, melting at 71°, which are volatile and dissolve in potash to a blue and in ammonia to a green solution.

Pyrogallo-quinone, $C_6H_4(O_2C_6H_3(OH)_2)_2$, is made in a similar way, and forms red needles insoluble in water and melting above 200°.

2. *Methyl quinone*, $CH_3.C_6H_3O_2$, from the oxidation of orthotoluidine, crystallises in yellow plates melting at 67° and forms

$$CH_3.C_6H_3(OH)_2,$$

m.p. 124°, on reduction with sulphurous acid.

3. A *xylo-quinone*, or *phlorone*, $C_8H_8O_2$, prepared by oxidation of beech-wood creasote, separates from water in yellow needles, melting at 60°.

4. *Dimethyl oxyquinone*, $(CH_3)_2C_6H(OH)O_2$, obtained from diamido-mesitylene, melts at 103°.

a-Propyl-methyl-quinone, $C_3H_7(CH_3)C_6H_2O_2$, prepared by the gentle oxidation of amido-thymol, melts at 45·5°, boils at 200°. It gives a sulpho-salt with potassic sulphite, and is reduced by sulphurous acid to $C_3H_7.C_6H_2(OH)_2.CH_3$. Chlorine and bromine derivatives have been obtained.

BENZENE TRI-SUBSTITUTION PRODUCTS.

997. A very limited number only of the very numerous known compounds coming under this category can be considered here.

They all come under the general formulæ $C_6H_3X_3$, $C_6H_3X_2Y$, and $C_6H_3.XYZ$, in which X, Y, and Z may denote the different halogens, nitryl, amido, hydroxyl, diazo-sulphon, &c., groups.

They may be named, according to the position of the substituting groups:

symmetrical = 1:3:5, *unsymmetrical* = 1:2:4,
and *consecutive* = 1:2:3.

Trihaloid Benzenes.—Trichlor-benzenes, $C_6H_3Cl_3$. The three isomers are known. The 1:3:5 modification, prepared from trichloraniline, melts at 63·4°, and crystallises in long needles, and boils at 208·5°.

1:2:4 trichlor-benzene, obtained by the direct action of chlorine on benzene, forms rhombic prisms, melting at 17° and boiling at 206°–210°. It is also obtained from $C_6Cl_6H_6$ by the action of potassic hydrate.

1:2:3 trichlor-benzene, obtained, together with the last, from the action of chlorine on metachlor-acetanilide and successively boiling the resulting trichlor-anilines with caustic soda and with potassic nitrite, forms large tables, melts at 53°–54°, and boils at 218°–219°.

Tribrom-benzenes, $C_6H_3Br_3$. The symmetrical modification, (1:3:5), obtained by the reaction between ethyl nitrite and tribromaniline, and from metadibrom-amido-benzene, melts at 119° and boils at 278°.

Unsymmetrical, (1:2:4), prepared by the decomposition of benzene hexabromide with potassic hydrate and by the direct action of bromine on benzene. It forms shining needles, melting at 44° and boiling at 275°.

Consecutive, (1:2:3), obtained from tribrom-amido-benzene by replacement of the amido group by hydrogen, crystallises in beautiful rhombic plates, melting at 87·4°.

Triiodo-benzene, $C_6H_3I_3$, prepared from benzene by means of iodic acid and iodine, forms needles melting at 76°.

The various *nitro-dibrom-benzenes* have already been mentioned under dibrom-benzenes (§ 982).

The following *nitro-dichlor-benzenes* are known, the position of the nitro group being taken as 1:—

1:2:4 forms needles, melts at 32°.
1:2:5 crystallises in tablets, melts at 55°.
1:3:4 forms long needles, melts at 43°.
1:3:5 crystallises in thin plates, melts at 64°–65°.

A nitro-diiodo-benzene, 1:2:4, is also known, which melts at 168°.

Dichlor-anilines, $C_6H_3Cl_2.NH_2$. Five of these bodies have been obtained by reduction of the corresponding dichlor-nitro-benzenes.

(1:2:3) melts at 23°–24°, boils at 252°.
(1:2:4), needles, melts at 62·5°, boils at 245°.
(1:2:5), colourless needles, melts at 20°.
(1:3:4), crystalline solid, melts at 71·5°, boils at 272°.
(1:3:5), white brittle needles, melts at 50·5°.

Dibrom-anilines, $C_6H_3Br_2.NH_2$.

1:2:4 crystallises in large flat rhombic prisms, melts at 79·4°.
1:2:5 crystallises in nodular groups of prisms, melts at 51°–52°.
1:3:4, colourless crystals, melts at 80·4°.
1:3:5, white needles, melts at 56·5°.
1:2:6 (?) has probably also been prepared.

Dinitraniline, $C_6H_3(NO_2)_2.NH_2$ [1:2:4], is prepared by the action of alkalies on dinitro-phenyl-citraconamide, and from the corresponding dinitro-chlor-benzene, by heating with ammonia. Ammonic sulphide converts it into nitro-phenylene-diamine:

$$C_6H_3(NO_2)_2.NH_2 + 3H_2S = C_6H_3(NO_2)(NH_2)_2 + 2OH_2 + 3S.$$

It forms greenish yellow tabular crystals, melting at 182°–183°, and does not combine with acids.

The isomeric (1:2:6) compound is obtained by heating the ethylic or methylic ether of dinitro-phenol with ammonia. It melts at 138° and crystallises in yellow needles.

998. *Substitution Products of Phenol.* — *Consecutive dichlor-phenol*, $C_6H_3Cl_2.OH$, 1:2:6(OH = 1), forms hexagonal needles, melts at 43°, and boils at 209°:

Unsymmetrical dichlor-phenol, 1:2:4, melts at 65° and boils at 219°.

A *dibrom-phenol*, 1:2:4, is formed by the direct action of bromine on phenol; it melts at 40°.

Diiodo-phenol, (1:2:4), melts at 150°.

Phenol disulphonic acid, 1:2:4, is readily obtained by treating phenol with excess of sulphuric acid.

It crystallises in deliquescent needles, and in solution gives a deep ruby red colour with ferric chloride.

Numerous tri-substitution derivatives of benzene are also known, containing three different groups or elements, but space will not allow of their description.

Triphenols, Trihydroxy-benzenes, $C_6H_3(OH)_3$.

999. *Pyrogallol,* or *pyrogallic acid,* metatrioxy-benzene, (1:2:4), is obtained by heating gallic acid in a stream of carbonic anhydride, or with water, at 210°:

$$C_6H_2.(OH)_3.CO.OH = CO_2 + C_6H_3(OH)_3.$$

It crystallises in colourless shining needles or plates, which dissolve easily in water ($2\frac{1}{2}$ parts) and melt at 115°. It is most easily oxidised in alkaline solutions, by simple exposure to the air, into carbonic and acetic acids and brown humus-like bodies. Its solutions reduce salts of gold, silver, and mercury, and give a deep blue coloration with ferrous salts.

An ethereal solution gives with ammonia a compound:

$$C_6H_3(OH)_2(ONH_4).$$

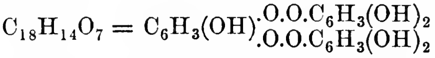
Treated with chlorine in acetic acid solution, two bodies:

$$C_{18}H_7Cl_{11}O_{10} \text{ and } C_{18}H_{10}Cl_{12}O_{14},$$

have been obtained, and with bromine $C_{18}H_4Br_{14}O_6$.

By the action of acetylic chloride a *triacetate,* $C_6H_3(O.C_2H_3O)_3$, is produced. It forms small crystals, which may be sublimed unchanged.

On very gentle oxidation, either with argentic nitrate, chromic acid, or permanganate, a body corresponding to hydro-quinone, and termed *purpurogallin:*



$$C_{18}H_{14}O_7 = C_6H_3(OH)\begin{array}{l}.O.O.C_6H_3(OH)_2\\ .O.O.C_6H_3(OH)_2\end{array}$$

is produced. It may be crystallised from alcohol, and then forms beautiful acid needles of m.p. 220°. It dyes mordanted fabrics red.

1000. *Phloro-glucol, paratrioxy-benzene,* (1:3:5), results from the decomposition of phloretin and quercetin with potassic hydrate solution, and by fusing potassic hydrate with gamboge, dragon's blood, moritannic acid, and several other bodies of this nature. It crystallises from aqueous watery solution in rhombic prisms of the formula $C_6H_3(OH)_3.2H_2O$. It loses all its crystal water at 100° and melts at 220°. It is soluble in water, alcohol, and ether, and gives a deep violet coloration with ferric salts. The *triacetate,* $C_6H_3(O.C_2H_3O)_3$, forms insoluble prisms.

On treatment with ammonia thin shining crystals of *phloramine* are produced, thus:

$$C_6H_3(OH)_3 + NH_3 = H_2O + C_6H_3(NH_2)(OH)_2.$$

Nitrous acid forms a substance of the composition $C_{12}H_8O_5$, termed phloreïn, which gives a deep purple solution with alkalies.

The following compounds of phloro-glucol have also been described :

Tribromide, $C_6Br_3(OH)_3$.
Trinitro-phloro-glucol, $C_6(NO_2)_3(OH)_3$.
Phloro-glucide, $C_{12}H_{10}O_5$.

Tetrasubstitution Derivatives of Benzene.

1001. All three possible tetrachlor-benzenes are known.

Symmetrical, (1:2:4:5), is obtained by the action of chlorine on benzene; it crystallises in needles, melts at 139°, and boils at 240°.

Unsymmetrical, (1:3:4:5), obtained from ordinary trichlor-aniline, melts at 150° and boils at 246°.

Consecutive, (1:2:3:4), produced from consecutive trichlor-aniline, crystallises in needles, melts at 46°, and boils at 254°.

Unsymmetrical tetrabrom-benzene, (1:3:4:5), is obtained by the action of phosphoric bromide on ordinary tribrom-phenol or from ordinary tribrom-aniline; it forms long needles, melting at 98·5°.

Another modification of as yet undetermined constitution has been obtained by the action of bromine on benzene; it melts at 140°.

Tribrom-phenol, (1:2:4:6), obtained directly by the action of bromine on phenol, forms colourless needles, which melt at 95°.

Triiodo-phenol, (1:2:4:6), obtained by the action of iodine and iodic acid on phenol, melts at 156°.

Two *trichlor-anilines* are known.

1:2:4:5, prepared by reducing the corresponding nitro-trichlor-benzene, forms colourless needles, melting at 96·5° and boiling at 270°.

1:2:4:6 is obtained by the action of chlorine on aniline; it crystallises in brilliant needles, melts at 77·5°, and boils at 260°.

Tribrom-anilines, $C_6H_2Br_3.NH_2$.

1:2:4:6, colourless needles, melting at 118°.

1:3:4:5 is crystalline, and appears to decompose below the temperature of fusion.

Trinitraniline, picramide, $C_6H_2(NO_2)_3.NH_2$ (1:2:4:6), is obtained by the action of ammonia on trinitrochlor-benzene or on ethylic picrate. It forms dark green or violet crystals, which melt at 188°.

The most important member of the group is

Trinitro-phenol, or Picric Acid, $C_6H_2(NO_2)_3.OH$ (1:2:4:6).

1002. Trinitro-phenol is obtained by the action of excess of nitric acid (finally assisted by heat) on phenol, on paranitro-phenol, on both dinitro-phenols, also on indigo, aniline, and many resins. It is difficultly soluble in cold water, more readily in hot water, alcohol, and ether, and crystallises in brilliant pale yellow prisms and plates; it melts at 122° and explodes on stronger heating.

Its solutions dye silk and wool of a permanent yellow colour. Its taste is intensely bitter, and it behaves to metallic compounds like a strong acid (hence the name *picric acid*). The salts crystallise well, are of a deep yellow colour, and explode with great violence on heating or percussion. *Potassic picrate*, $C_6H_2(NO_2)_3OK$, forms needles difficultly soluble in water, whilst the sodic, ammonic, and baric salts are difficultly soluble.

Picric acid also yields peculiar crystallisable compounds with many hydrocarbons belonging to the aromatic group; e.g. with one molecule of benzene, but especially with naphthalene, anthracene, &c.

With chloride of lime it yields chlorpicrin (§ 542); with phosphoric chloride it reacts according to the equation:

$$C_6H_2(NO_2)_3.OH + PCl_5 = POCl_3 + HCl + C_6H_2(NO_2)_3Cl,$$

yielding *trinitro-chlor-benzene*, forming needles melting at 83°, which are reconverted into picric acid by water and by ammonia into *picramide* or *trinitraniline* (comp. last section).

On passing sulphuretted hydrogen into an alcoholic solution of ammonic picrate, sulphur separates, and, according to the equation:

$$C_6H_2(NO_2)_3.O.NH_4 + 3H_2S = S + 2H_2O \\ + C_6H_2(NO_2)_2(NH_2).O.NH_4,$$

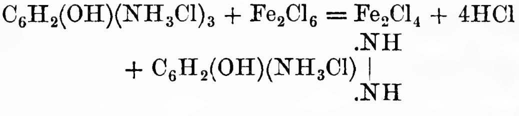
the ammonic salt of *picramic acid* is formed, from which acetic acid liberates the free acid as *dinitro-amido-phenol*, $C_6H_2(NO_2)_2(NH_2).OH$, forming red needles of acid properties melting at 165°.

In aqueous solution, on the other hand, six molecules of sulphuretted hydrogen react on ammonic picrate, yielding *diamido-nitro-phenol*, $C_6H_2(NO_2)(NH_2)_2.OH$, crystallising in dark yellow needles or plates and yielding saline compounds with both acids and bases.

By the action of tin and hydrochloric acid on phenol, when heated, a crystalline stannous chloride double salt separates, which, by decomposition with sulphuretted hydrogen and evaporation of the filtrate, yields colourless needles of *triamido-phenol hydrochloride*:

$$C_6H_2(NH_2.HCl)_3.OH,$$

readily soluble in water, difficultly in hydrochloric acid, from which triamido-phenol cannot be separated unchanged. By mixing with solution of ferric chloride yellowish brown needles with bluish lustre separate of *amido-hydrazo-phenol hydrochloride*, which dissolve with bluish colour in water. The reaction proceeds according to the equation:



$$C_6H_2(OH)(NH_3Cl)_3 + Fe_2Cl_6 = Fe_2Cl_4 + 4HCl \\ + C_6H_2(OH)(NH_3Cl)\begin{array}{l}.NH \\ | \\ .NH\end{array}$$

By slow addition of a hot solution of one part of picric acid in nine parts of water to a solution of two parts of potassic cyanide in four parts of water heated to 60°, a red colour is developed, and on cooling brownish red scales of metallic green lustre separate of *potassic picro-cyamate* or *isopurpurate*, $C_8H_4KN_5O_6$ (comp. § 922), which are little soluble in cold, but readily in hot water, and dissolve in alcohol with deep red colour, and in the dry state explode violently on heating. The free isopurpuric acid has not yet been obtained.

Penta Substitution Derivatives of Benzene.

1003. The chlorine and bromine compounds are known; they both crystallise in needles. *Pentachlor-benzene*, C_6HCl_5, melts at 85° and boils at about 270°; *pentabrom-benzene* does not melt at 240°.

Trinitro-resorcin, $C_6H(NO_2)_3(OH)_2$, also known as *oxypicric* *acid* or *styphnic acid*, is obtained by the action of cold nitric acid on resorcin, and from moritannic acid, many gum resins (e.g. galbanum, ammoniacum), also from the extracts of Brazil and Sapan woods by boiling with nitric acid. It crystallises in yellow hexagonal plates or prisms, melts at 175°, and can be sublimed by careful heating, but explodes on quick heating. It is difficultly soluble in water, readily in alcohol and ether, and behaves as a strong dibasic acid, whose salts, $C_6H(NO_2)_3(OM)_2$, crystallise well and are explosive.

Tetrabrom-aniline, $C_6HBr_4.NH_2$ (1:2:3:4:6), is formed by the action of excess of bromine on metabrom-aniline, or on the dibrom-anilines, (1:2:4) or (1:3:6); it crystallises in needles, melting at 115·3°.

Hexa Substitution Derivatives of Benzene.

1004. *Hexachlor-benzene*, C_6Cl_6, also termed *perchlor-benzene* or *Julin's chloride of carbon*, is the last product of the action of chlorine on benzene, especially when assisted by antimonic chloride at the boiling temperature. It is obtained synthetically by passing the vapours of chloroform or tetrachlor-ethylene through red-hot tubes:

$$6CHCl_3 = 6HCl + 3Cl_2 + C_6Cl_6$$

$$3C_2Cl_4 = 3Cl_2 + C_6Cl_6,$$

and from acetylene tetrachloride (§ 752) at 360°:

$$3C_2H_2Cl_4 = 6HCl + C_6Cl_6.$$

It crystallises in colourless prisms, melting at 222°–226° and boiling at about 330°.

Hexabrom-benzene is prepared by the action of bromine in presence of iodine on benzene. It resembles the chlor compound, but melts at above 310°, crystallises in needles, and can be sublimed.

Pentabrom-aniline, $C_6Br_5(NH_2)$, is formed by the action of bromine on symmetric dibrom-aniline. It crystallises in transparent needles and does not melt at 222°.

Quinone and Hydroquinone Derivatives.

1005. *Tetrachlor-quinone*, or *chloranil*, $C_6Cl_4O_2$, is obtained, together with trichlor-quinone, by the chlorination of quinone, or still better by careful treatment of aniline, salicylic acid, or phenol with hydrochloric acid and potassic chlorate. It crystallises in brilliant yellow plates, readily soluble in boiling alcohol, which can be sublimed undecomposed, and is converted by phosphoric chloride into hexachlor-benzene.

Tetrachlor-quinone dissolves with purple-red colour in hot potassic hydrate solution, and on cooling purple-red crystals of *potassic chloranilate*, $C_6Cl_2O_2(OK)_2,H_2O$, separate, from which sulphuric acid liberates *chloranilic acid*, crystallising in reddish white scales of the formula $C_6Cl_2O_2(OH)_2,H_2O$.

Sulphurous acid converts chloranil into *tetrachlor-hydroquinone*:

$$C_6Cl_4O_2 + 2H_2O + SO_2 = H_2SO_4 + C_6Cl_4(OH)_2.$$

Chloranilic acid, on heating at 100° in closed vessels with sulphurous acid, is converted into *hydrochloranilic acid* or *dichlor-tetrahydroxybenzene :*

$$C_6Cl_2O_2(OH)_2 + 2H_2O + SO_2 = H_2SO_4 + C_6Cl_2(OH)_4.$$

Hydrochloranilic acid crystallises in white needles; when exposed to air in a damp condition it is reconverted into chloranilic acid; with chloracetyl it yields a crystalline acetate, $C_6Cl_2(O.C_2H_3O)_4$, which melts unaltered at 235°.

1006. *Tetrabrom-quinone*, or *bromanil*, $C_6Br_4O_2$, is obtained by adding 1 part of phenol to a mixture of 10 parts of bromine and 3½ parts of iodine placed under water; after heating for two hours the crude product is extracted with carbonic disulphide, when bromanil remains undissolved. It crystallises in golden yellow plates and behaves similarly to chloranil.

1007. *Tetrabrom-pyrocatechin*, $C_6Br_4(OH)_2$, is obtained by rubbing together pyrocatechin and excess of bromine; it crystallises in brownish red needles, insoluble in water.

Tribrom-pyrogallol, $C_6Br_3(OH)_3$, is prepared from pyrogallol by action of bromine; it forms flat yellow-coloured needles, which dissolve in boiling water.

HOMOLOGUES OF BENZENE, OR ALKYL BENZENES, C_nH_{2n-6}.

1008. The homologues of benzene are produced by the replacement of one or more of the hydrogen atoms in benzene itself by the alcohol radicals of the C_nH_{2n+1} series. They combine the properties of the benzene and of the ethane series of hydrocarbons.

In the case of *methyl-benzene* or *toluene*, $C_6H_5.CH_3$, only one modification is known, but with the higher members of the series the number of isomers may be very large, the diversity arising partly from isomerism in the substituting alkyl group itself, and partly from position isomerism (in the case of di and tri derivatives) in the benzene nucleus.

The following table shows all the compounds of the group known at present :—

	Monalkyl Benzenes	Dialkyl Benzenes	Trialkyl Benzenes	Tetra-alkyl Benzenes
C_7H_8	$C_6H_5.CH_3$ Toluene			
C_8H_{10}	$C_6H_5.C_2H_5$ Ethyl benzene	$C_6H_4(CH_3)_2$ O.-, p.-, and m.-xylenes		
C_9H_{12}	$C_6H_5.C_3H_7$ Propyl benzene Isopropyl benzene	$C_6H_4\left\{\begin{matrix}CH_3\\C_2H_5\end{matrix}\right.$ Ethyl-methyl benzene	$C_6H_3(CH_3)_3$ Mesitylene, (1 : 3 : 5) Pseudocumene, (1 : 3 : 4)	
$C_{10}H_{14}$	$C_6H_5.C_4H_9$ Isobutyl benzene	$C_6H_4\left\{\begin{matrix}CH_3\\C_3H_7\end{matrix}\right.$ P.- and m.-propyl-methyl benzene Isopropyl-methyl benzene $C_6H_4(C_2H_5)_2$ P.-diethyl benzene	$C_6H_3(C_2H_5)(CH_3)_2$ Ethyl-dimethyl benzene, (1 : 3 : 4) and (1 : 3 : 5)	$C_6H_2(CH_3)_4$ Tetramethyl benzene (durene)
$C_{11}H_{16}$	$C_6H_5.C_5H_{11}$ Isoamyl benzene $C_6H_5.CH(C_2H_5)_2$ Diethyl carbin-benzene		$C_6H_3(C_3H_7)(CH_3)_2$ Propyl-dimethyl benzene Isopropyl-dimethyl benzene $C_6H_3(C_2H_5)_2.CH_3$ Diethyl-methyl benzene	
$C_{12}H_{18}$	$C_6H_5.C_6H_{13}$ Isohexyl benzene	$C_6H_4(C_5H_{11}).CH_3$ Isoamyl-methyl benzene	$C_6H_3(C_2H_5)_3$ Triethyl benzene	$C_6(CH_3)_6$ Hexamethyl benzene
$C_{13}H_{20}$			$C_6H_3(C_5H_{11})(CH_3)_2$ Isoamyl-dimethyl benzene $C_6H_3(C_3H_7)_2.CH_3$ Dipropyl-methyl benzene	

MONALKYL BENZENES, $C_6H_5.C_nH_{2n+1}$.

1009. The monalkyl benzenes may all be obtained synthetically—(1) by the action of sodium on a mixture of a monohaloid benzene with monohaloid or paraffin diluted with perfectly dry ether:

$$C_6H_5Br + Br.C_nH_{2n+1} + Na_2 = 2NaBr + C_6H_5.C_nH_{2n+1};$$

(2) by distillation of calcic salts of acids of the benzoic series with excess of lime.

As far as is yet known they are all liquids. The monalkyl derivatives yield on oxidation benzoic acid; e.g.

$$C_6H_5.CH_3 + 2CrO_3 = Cr_2O_3 + OH_2 + C_6H_5.CO.OH;$$

whilst the homologues give benzoic acid and also carbonic anhydride from the complete oxidation of the alkyl nucleus:

$$C_6H_5.C_nH_{2n+1} + 2nCrO_3 = nCr_2O_3 + (n-1)CO_2 + nH_2O \\ + C_6H_5.CO.OH.$$

Toluene, Methyl-benzene, $= O_6H_3CH_3$.

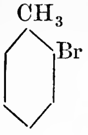
1010. Toluene may be obtained from that portion of coal-tar oil boiling between 100° and 120°; from brom-benzene methyl iodide and sodium; by dry distillation of the calcic salts of the toluic acids and of tolu-balsam, and from benzylic alcohol by the action of strong alkalies. It is a colourless liquid of sp. gr. ·882 at 0°, boiling at 111°. It gives benzoic acid on oxidation.

Substitution Products of Toluene.

1011. The substitution derivatives of toluene are much more numerous than those of benzene, the mono products alone giving, in addition to ortho, meta, and para isomers, a fourth, in which a hydrogen atom of the methyl group is replaced; e.g.

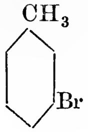
Brom toluenes.

Ortho.



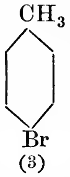
(1)

Meta.



(2)

Para.



(3)

Benzyl bromide.

(4)

The bodies obtained by substitution as in (4) scarcely belong to the aromatic group, their properties being more closely allied to those of the alkyl compounds. They will therefore be described separately.

The constitution of the mono-substituted toluenes is generally settled by converting them into the benzene dicarbonic acids. For example, the three brom-toluenes are converted by treatment with methylic iodide and sodium into the corresponding ortho-, meta-, and para-dimethyl-benzenes:

$$C_6H_4Br.CH_3 + ICH_3 + Na_2 = NaI + NaBr + C_6H_4(CH_3)_2.$$

Of these the para product is converted by oxidation first into paratoluic acid, $C_6H_4(CH_3).CO.OH$, and further into terephthalic acid, $C_6H_4(CO.OH)_2$.

The meta product similarly yields isophthalic acid with chromic acid, whilst orthodimethyl-benzene is oxidised to orthotoluic acid by dilute nitric acid and is totally destroyed by chromic acid.

The relationship of the nitro and amido compounds to the phthalic acids can be determined in similar manner, as they can be easily converted, by means of the diazo compounds, into the corresponding bromine derivatives.

1012. *Haloid Toluenes.*—Chlorine and bromine act directly on toluene, forming substitution derivatives, the place of substitution depending on the temperature employed. When well cooled, or in the presence of iodine and some other substances, the halogen displaces hydrogen from the aromatic or benzene nucleus. At a temperature approaching the boiling point the substitution is almost entirely at the methyl group.

The following table gives some of the most important chloro and bromo derivatives of toluene :—

			M.p.	B.p.
$C_6H_4.CH_3.Cl$	monochlor-toluene	ortho	liquid	157°
		meta	liquid	156°
		para	6·5°	160·5°
$C_6H_3Cl_2.CH_3$	dichlor-toluene		liquid	196°
$C_6H_2Cl_3.CH_3$	trichlor-toluene		76°	235°
$C_6HCl_4.CH_3$	tetrachlor-toluene		91°	271°
$C_6Cl_5.CH_3$	pentachlor-toluene		218°	301°
$C_6H_4Br.CH_3$	brom-toluene	para	28·5°	184·6°
		meta	liquid	184·5°
		ortho	liquid	182°

In addition to these six isomeric dibrom-toluenes, $C_6H_3.Br_2.CH_3$, are known, one, or possibly two, of which may be obtained by the direct action of bromine on toluene, the remainder from various brom-amido-toluenes by means of the diazo reaction (comp. § 982).

Two tribrom-toluenes have also been similarly obtained. One is a liquid boiling at 260°, the other a solid of m.p. 70° and b.p. 290°.

Few iodo-toluenes are known.

Ortho- and *meta-iodo-toluene*, $C_6H_4I.CH_3$, are liquids boiling at 204° and 205° respectively. The *para* body melts at 35° and boils at 211°. They are all obtained by the action of hydriodic acid on the azo-toluenes.

1013. *Nitro-toluenes.*—On treating toluene with fuming nitric acid a mixture of ortho- and *para-nitro-toluene* is produced, from which the latter may be separated by freezing and subsequent fractional distillation. It melts at 54° and boils at 236°.

Pure *ortho-nitro-toluene* may be obtained from amido-nitro-toluene, $C_6H_3(NH_2).(NO_2).CH_3$, by the diazo reaction (comp. § 976); it is liquid and boils at 223°.

Metanitro-toluene is obtained by nitrating acetyl paramido-toluene, $C_6H_4(CH_3).NH(C_2H_3O)$, conversion into the diazo compound, and reduction of this by heating with alcohol (§ 976). It boils at 231°.

Dinitro-toluenes, $C_6H_3(NO_2)_2CH_3$. Ortho- and para-nitro-toluene, on treatment with very concentrated nitric acid, give a *dinitro-toluene*, melting at 70·5°. The substituting groups have the positions:

$$CH_3:NO_2.NO_2\ 1:2:4.$$

Another isomer is obtained from ortho-nitro-toluene. It is liquid.

Metanitro-toluene gives an isomer which forms colourless needles, melting at 60°.

Two *trinitro-toluenes* are known. The one obtained by direct nitration of mono- and dinitro-toluenes melts at 80·5° and appears to have the positions 1:2:4:6.

1014. *Amido-toluenes, toluidines,* $C_6H_4(NH_2).CH_3$. The three nitro-toluenes on reduction yield the respective amido-toluenes.

Ortho-toluidine is a liquid boiling at 197° and not solidifying at − 20°. On treatment of its aqueous solution with bleaching powder an oxidation product is formed, which gives a fine red coloration with dilute acids.

Acetyl ortho-toluidine, $C_6H_4(CH_3).N(C_2H_3O)H$, is moderately soluble in water and melts at 107°.

Metatoluidine boils at 197°; its acetyl derivative melts at 65·5°.

Paratoluidine forms beautiful crystals melting at 45° and boiling at 198°. Its acetyl derivative melts at 145°. It gives no colour reaction with bleaching powder solution. Paratoluidine is also produced by heating methyl aniline hydrochloride to 350°:

$$C_6H_5.N(CH_3)H_2Cl = C_6H_4(CH_3).NH_3Cl.$$

The amido-toluenes yield similar derivatives to the amido-benzenes —e.g. ureas, sulphureas, guanidines, &c.

Diamido-toluene, toluylene-diamine, $C_6H_3.(NH_2)_2CH_3$, is obtained by the reduction of 1:2:4 dinitro-toluene, melting at 70·5°. It crystallises from boiling water, alcohol, and ether in large prisms, melting at 99° and boiling at 280°.

1015. *Hydroxy-toluenes,* $C_7H_7.OH$. Four of these bodies are known.

Methyl-phenols, cresols, $C_6H_4(OH)CH_3$. The crude phenol from coal-tar oil contains a mixture of all three cresols, para, ortho, and meta. The two former are obtained from dipotassic salts of para- and ortho-toluene-sulphonic acids by fusion with alkalies, and also from the corresponding diazo compounds (§ 976).

Metacresol may be obtained by distilling the calcic salt of oxy-uvitic acid, $C_6H_2(OH).(CH_3).(CO.OH)_2$, and by the action of phosphoric anhydride on thymol, when a meta-cresol phosphate is formed, which is decomposed by treatment with potash and the cresol extracted by ether. Carvacrol (§ 1023), the isomer of thymol, gives ortho-cresol under the same circumstances.

The cresols behave like the phenols, forming metallic derivatives with bases which react with the alkyl haloid compounds, giving ethers; e.g.

$$C_6H_4(CH_3).OK + IC_2H_5 = KI + C_6H_4(CH_3).O.C_2H_5.$$

They also form acetates with acetylic chloride:

$$C_6H_4(CH_3).O.C_2H_3O.$$

Orthocresol is a white solid, melting at 31° and boiling at 185°–186°.

Metacresol is a liquid boiling between 195° and 200°.

Paracresol melts at 36° and boils at 198°. It is a white crystalline substance.

The fourth modification, benzyl alcohol, $C_6H_5.CH_2.OH$, is considered elsewhere (§ 1027).

1016. *Dihydroxy-toluenes,* $C_7H_8O_2 = C_6H_3(CH_3)(OH)_2$.

Several isomers are known, but they have not been well investigated.

1. *Orcin, orcinol,* $C_6H_3(CH_3)(OH)_2$ (1:3:5?), is obtained by heating the acids derived from several varieties of lichens, as orsellinic acid, $C_8H_8O_4 = C_6H_2(CH_3)(OH)_2.CO.OH$, lecanoric acid, $C_{16}H_{14}O_7$, erythric acid, $C_{20}H_{22}O_{10}$, with alkalies, or better with milk of lime. After saturating with carbonic acid the orcinol may be extracted by ether.

Orcin forms large monoclinic crystals of the composition :

$$C_7H_8O_2,OH_2,$$

which melt at 58°, and after the water has been driven off at 86°, and boil at 290°. Ferric chloride colours its aqueous solutions violet. It has a sweet, astringent taste, and when heated with acetylic chloride forms a compound, $C_6H_3(CH_3).(O.C_2H_3O)_2$, melting at 25°.

Orcin has been obtained by fusing potassic orthochlor-toluene sulphonate with potassic hydrate. It yields a crystalline compound with ammonia, which is rapidly oxidised in the air to *orceïn*, $C_7H_7NO_3$, a brownish red substance, dissolving in alkalies to a deep purple solution, from which acetic acid precipitates a colouring matter apparently identical with the litmus from *Lecanora tartarea.*

Several haloid and nitro derivatives of orcinol are known.

Monobrom-orcin, $C_7H_5Br(OH)_2$.

Tribrom-orcin, $C_7H_3Br_3(OH)_2$, m.p. 103°.

Pentabrom-orcin, $C_7Br_5(OH)_2$, m.p. 126°.

A *trichlor-orcin,* $C_7H_2Cl_3(OH)_2$, melting at 123°, and a *pentachlor-orcin,* $C_7HCl_5(OH)_2$, m.p. 120·5°, and two *iodo-orcins* are known.

Two *mononitro-orcins,* $C_7H_5(NO_2)(OH)_2$, have been obtained; α m.p. 120, β m.p. 115°.

Trinitro-orcin, obtained by the action of cold fuming nitric acid on orcin, forms large yellow prisms, melting at 162°. It acts as a strong dibasic acid.

2. *Isomeric Orcinols.*—The potassic salts of the two toluene-disulphonic acids, obtained when toluene is heated with sulphuric acid, give an *iso-orcin* on fusion with potash, which melts when anhydrous at 87° and boils at 270°. It is unaltered in the air.

Homopyro-catechin is obtained by the action of hydriodic acid on *creosol:*

$$C_6H_3(CH_3).(OH)OCH_3 + HI = CH_3I + C_6H_3(CH_3).(OH)_2.$$

It is a colourless oil boiling at 219°, and is found along with several of its homologues in beech-wood tar. It has been very little investigated.

1017. *Toluene-sulphonic acids,* $C_6H_4.(CH_3)(SO_2.OH)$. The *ortho* and *para* acids are produced by dissolving toluene in fuming sulphuric acid. They may be separated by means of their potassic salts, the para compound being the more insoluble.

Metatoluene sulphonic acid is obtained by reduction of orthochlortoluene metasulphonic acid by means of sodium amalgam.

Homologues of Toluene.

1018. *Ethyl-benzene*, $C_6H_5.C_2H_5$, is obtained by the action of sodium on a mixture of brom-benzene and ethylic bromide, or by heating ethylic chloride and benzene in the presence of aluminic chloride.

It is a colourless liquid, of b.p. 134° and sp. gr. ·8664. On oxidation benzoic acid is produced. Chlorine acts on boiling ethyl benzene, forming *phenethyl chloride*, $C_6H_5.CH_2.CH_2Cl$. At the ordinary temperature the chlorine enters the aromatic nucleus. With bromine, however, the reverse reaction appears to take place to a great extent, β-phenethyl bromide :

$$C_6H_5.CHBr.CH_3,$$

being formed.

Several nitro derivatives have been formed (§ 1013).

Paranitro-ethyl benzene, b.p. 245°–246° ; *ortho*, b.p. 227°–228°.

They yield corresponding *amido-ethyl benzenes*, $C_6H_4(NH_2).C_2H_5$, on reduction.

With concentrated sulphuric acid ethyl benzene gives two sulphonic acids, $C_6H_4(SO_2OH).(C_2H_5)$. The one formed in largest quantity on fusion with potash gives an *ethyl phenol*, $C_6H_4(OH)C_2H_5$, which melts at about 47° and boils at 210°. It is not known for certain if it be the para or ortho product.

Phlorol, which is obtained by the distillation of phloretic acid with lime, appears to be an isomer of ethyl phenol, but its constitution is as yet uncertain. It is a liquid boiling at 220° which does not solidify at $-18°$.

Coal and beech-wood tar also contain phenols of the formula $C_8H_{10}O$, which, however, are not well known. They give, on distillation with oxidising agents, a quinone, *phlorone*, $C_8H_8O_2$, which sublimes in light yellow needles and is converted by nascent hydrogen into *hydrophlorone*, $C_8H_8(OH)_2$, forming easily soluble colourless crystals.

1019. *Propyl-benzene*, $C_6H_5.CH_2.CH_2.CH_3$, has been obtained synthetically by the action of sodium on a mixture of α-iodo-propane and monobrom-benzene. It boils at 157°. *Isopropyl benzene*, similarly obtained, and also prepared from cumic acid by distillation with lime :

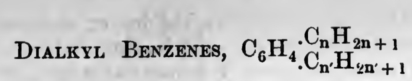
$$[C_6H_4(C_3H_7)^{\beta}.CO.O]_2Ca + Ca(OH)_2 = 2CaCO_3 \\ + 2C_6H_5.CH.(CH_3)_2,$$

boils at 151°, and hence is termed *cumene*. They both yield benzoic acid on oxidation.

Isobutyl benzene, $C_6H_5.CH_2.CH(CH_3)_2$, is a colourless oil, boiling at 160°.

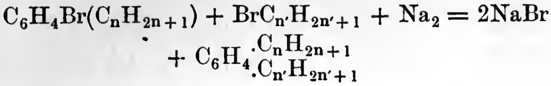
Isoamyl benzene, $C_6H_5.CH_2.CH_2.CH(CH_3)_2$, boils at 193°.

Isohexyl benzene, $C_6H_5.CH_2.CH_2.CH_2.CH(CH_3)_2$, prepared by the action of sodium on benzylic chloride and isoamylic bromide, boils at 214°.



DIALKYL BENZENES, $C_6H_4\begin{matrix}.C_nH_{2n+1}\\.C_{n'}H_{2n'+1}\end{matrix}$

1020. Dialkyl benzenes may be obtained from the monobrom substitution products of the monalkyl benzenes in a similar manner to the production of the latter from brom-benzene itself:

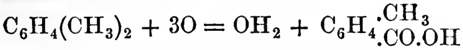


$$C_6H_4Br(C_nH_{2n+1}) + BrC_{n'}H_{2n'+1} + Na_2 = 2NaBr + C_6H_4\begin{matrix}.C_nH_{2n+1}\\.C_{n'}H_{2n'+1}\end{matrix}$$

The dibrom-benzenes also yield the same bodies to some extent:

$$C_6H_4Br_2 + 2BrC_nH_{2n+1} = 2Na_2 = 4NaBr + C_6H_4(C_nH_{2n+1})_2.$$

The dimethyl compounds, when submitted to the action of dilute nitric acid, give methyl-benzoïc acids; e.g.



$$C_6H_4(CH_3)_2 + 3O = OH_2 + C_6H_4\begin{matrix}.CH_3\\.CO.OH\end{matrix}$$

Chromic acid, however, oxidises the para compounds to terephthalic acid, the meta compounds to isophthalic acid:

$$C_6H_4(CH_3)_2 + 3O_2 = 2OH_2 + C_6H_4(CO.OH)_2,$$

the ortho compounds being completely destroyed.

When acted upon at their boiling points by the halogens, substitution products are formed, having the halogen in the alkyl group:

$$C_6H_4(CH_3)_2 + Cl_2 = C_6H_4(CH_3).CH_2Cl + HCl.$$

When kept cold, however, or in the presence of iodine, substitution takes place at the benzene nucleus:

$$C_6H_4(CH_3)_2 + Br_2 = C_6H_3Br(CH_3)_2 + HBr.$$

Fuming nitric acid forms nitro substitution products, in which the substitution has taken place on the benzene group, which may be reduced by nascent hydrogen to azo and amido products, and these in their turn converted by means of nitrous acid into diazo compounds.

Dimethyl Benzenes, Xylenes, $C_8H_{10} = C_6H_4(CH_3)_2$.

1021. Light coal-tar oil gives, on distillation, a fraction boiling between 136° and 139°, consisting of a mixture of meta- and paraxylene, which cannot be separated by fractional distillation.

Orthoxylene = 1:2 is prepared synthetically by the action of sodium on a mixture of orthobrom-toluene and methylic iodide diluted with ether. It is a colourless oil, boiling between 140° and 141°. With dilute nitric acid it is oxidised to orthotoluic acid. On heating for some time with a mixture of fuming nitric and sulphuric acids, trinitro-orthodimethyl benzenes are produced. Paraxylic acid also gives orthoxylene on distillation with lime or baryta.

Metaxylene, (1:3), is obtained pure by the distillation of xylic or mesitylenic acids with lime. It boils at 137°, is not attacked by dilute nitric acid, but is converted by chromic acid into isophthalic acid.

Paraxylene, (1:4), prepared by the action of sodium on crystalline parabrom-toluene mixed with methylic iodide and benzene, or from paradibrom-benzene and methylic iodide, crystallises in colourless monoclinic prisms, melting at 15° and boiling at 136°–137°. It gives paratoluic acid on oxidation with dilute nitric acid, and terephthalic acid with chromic acid.

Halogen Compounds of Xylenenes.—Brom-paraxylene :

$$C_6H_3Br(CH_3)_2,$$

forms shining tables, melting at 10° and boiling at 200°. By the further action of bromine a *dibrom-paraxylene*, $C_6H_2Br_2(CH_3)_2$, is produced, forming colourless plates, melting at 72°, boiling at 256°.

An isomeric body has been obtained of the constitution:

$$C_6H_4(CH_2Br)_2,$$

which melts at 146°.

Brom-metaxylene, $C_6H_3Br(CH_3)_2$, is liquid, boiling at 205°. A tetra-brom derivative, $C_6Br_4(CH_3)_2$, melting at 241°, is also known.

Nitro Derivatives.—Nitro-paraxylene, $C_6H_3(NO_2)(CH_3)_2$, is a colourless liquid, boiling at 235°–237°. Two isomeric dinitro bodies are known, one melting at 93°, the other at 125°. The latter is somewhat insoluble in alcohol, and may be separated from the one of lower melting point by this means. *Trinitro-paraxylene* melts at 137°.

Nitro-metaxylene melts at 2° and boils at 237°–239°.

Amido-metaxylene, $C_6H_3(NH_2)(CH_3)_2$, is also liquid and boils at 216°.

Dinitro-metaxylene melts at 93° and forms colourless flattened needles.

Xylidines, $C_6H_3(NH_2)(CH_3)_2$. Three liquid isomers are known. The metaxylidine boils at 216°. Paraxylidine boils at 220°–221°.

Dimethyl Phenols, $C_6H_3(CH_3)_2OH$, *Xylenols.*—Two isomers are known, and may be obtained from the coal-tar xylol mixture of oils by conversion into the sulphonic acids and fusion of these with potassic hydrate. Coal-tar xylenol consists principally of the meta compound, and yields metadimethyl oxybenzene, a soluble solid, melting at 75° and boiling at 216°. When acted on by bromine, a dibromide, melting at 81°, is produced. The potassic salt of mesitylene sulphonic acid, when fused with potash, also gives metaxylenol. The other isomeric xylenol is liquid and boils between 211°–212°.

It is also very likely that the phenols of the formula $C_8H_{10}O$, obtainable from heavy coal-tar oils (§ 1018), are xylenols, in which case phlorone may be a dimethyl quinone, $C_6H_2(CH_3)_2O_2$.

1022. *Ethyl-methyl benzenes*, $C_7H_{12} = C_6H_4\begin{smallmatrix}.CH_3\\.C_2H_5\end{smallmatrix}$. *Meta-ethyl-methyl benzene* is obtained from metabrom-toluene and ethylic iodide by the action of sodium. It boils between 158° and 159°.

Para-ethyl-methyl-benzene boils at 161°–162°, and does not solidify at $-18°$.

1023. *Dialkyl benzenes*, $C_{10}H_{14}$. 1. *Paradiethyl benzene :*

$$C_6H_4(C_2H_5)_2,$$

from parabrom-ethyl benzene, ethylic bromide, and sodium, is a liquid boiling between 178° and 179°. It gives ethyl-benzoic acid on oxidation.

2. *Cymene, parapropyl-methyl benzene,* $C_6H_4{}^{.CH_3}_{.C_3H_7}$ (1:4), is contained in various ethereal oils—e.g. Roman cumin oil, from the seeds of *Cuminum Cyminum,* in oil of nutmeg, oil of *Cicuta virosa,* or water hemlock, &c. It may be obtained from some terpenes, $C_{10}H_{16}$, by the long-continued action of iodine or by heating camphor with phosphoric anhydride or pentasulphide, or with zinc chloride:

$$C_{10}H_{16}O = OH_2 + C_{10}H_{14}.$$

It may also be obtained synthetically from primary propylic iodide and parabrom-toluene by the action of sodium.

Cymene is a colourless oil, boiling at 175° with an odour faintly recalling that of lemons. It gives paratoluic acid, $C_6H_4(CH_3).CO.OH$, on oxidation with dilute nitric acid. Fuming nitric acid converts it into a mixture of nitro-cymenes, of which one is liquid and volatile in a current of steam and another solid (m.p. 125°) and non-volatile.

With concentrated sulphuric acid a cymene sulphonic acid is produced, which gives *cymophenol,* $C_6H_3(OH){}^{.CH_3}_{.C_3H_7}$, on fusion with alkalies. It is a thick oil, boiling at 232°.

The same body is also produced when camphor is heated with iodine:

$$C_{10}H_{16}O + I_2 = 2HI + C_{10}H_{14}O.$$

Thymol, $C_6H_3(CH_3)(C_3H_7{}^{a}).OH$, is a propyl-methyl-phenol isomeric with carvacrol. It is obtained from oil of thyme by shaking with aqueous alkalies. It forms large crystals, melting at 44° and boiling at 230°. Nearly insoluble in water, but dissolving easily in alcohol and ether.

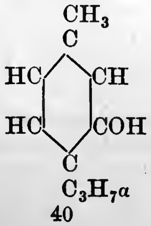
On heating with phosphoric anhydride metacresol phosphate and propylene are formed. With phosphoric sulphide *thio-thymol,* $C_6H_3.SH{}^{.CH_3}_{.C_3H_7}\,a$, b.p. 233°–235°, is produced.

On oxidation with manganic oxide and sulphuric acid, *thymoquinone,* $C_6H_2O_2{}^{.CH_3}_{.C_3H_7}\,a$, results.

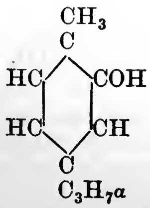
It forms yellow needles of a pungent odour, melting at 45·5°. Sulphites reduce it to *thymhydroquinone,* $C_6H_2(OH)_2{}^{.CH_3}_{.C_3H_7}$.

Carvacrol, the isomer of thymol, is obtained by the action of phosphoric acid on carvol, a substance contained in Roman oil of caraway; by heating camphor with one-third of its weight of iodine; and from paramethyl-propyl-benzene sulphonic acid by fusion with potash.

It is probable that in thymol the hydroxyl occupies the meta position with regard to the methyl, whilst in carvacrol it occupies the ortho position:



thymol



Metacymene, $C_6H_4(CH_3).C_3H_7$ (1:3), is prepared by the action of sodium at 0° on an ethereal solution of propyl-bromide and meta-brom-toluene. It is a colourless liquid, boiling at 176°.

Isocymene, paramethyl-isopropyl benzene, $C_6H_4(CH_3).CH:(CH_3)_2$, (1:4), is formed by the action of sodium on an ethereal solution of methylic iodide and parabrom-cumene. It is a colourless liquid, boiling at 217° and of sp. gr. 1·3014 at 15°.

$C_{12}H_{16}$, *paramethyl-isoamyl benzene*, 

$$C_6H_4\begin{matrix}.CH_3\\.CH_2.CH_2.CH(CH_3)_2\end{matrix},$$

boils at 213°.

TRIALKYL BENZENES, C_9H_{12}.

1024. Two isomeric trimethyl benzenes occur in that portion of coal-tar oil boiling between 163° and 168°. Although they cannot be separated by distillation alone, their different constitution has been pretty well established from their derivatives.

1. *Mesitylene*, $C_6H_3(CH_3)_3 = 1 . 3 . 5$, is formed when two volumes of acetone are distilled with one volume of sulphuric acid from retorts half filled with sand or pumice stone. The mesitylene is separated from ortho products by washing with sodic hydrate and repeated fractional distillation over metallic sodium. The coal-tar oil boiling between 160° and 170° is principally mesitylene.

It is a colourless liquid of high refractive power and pleasant odour, boiling at 163°. The relative position of the methyl groups, given as 1:3:5, is founded on the assumption that the three acetone molecules taking part in the formation of mesitylene behave similarly (§ 954), and also that no isomeric mono-substitution derivatives can be obtained where substitution has taken place in the benzene nucleus only.

On heating with phosphonic iodide to 250° it is converted into a hydrocarbon of the formula C_9H_{18}, b.p. 138°, which gives the same products on gentle oxidation as mesitylene—e.g. mesitylenic, uvitic, and trimesic acids.

Halogen and fuming nitric acid replace the benzene hydrogen in mesitylene very easily, but as yet no isomers have been obtained with certainty which supports to some extent the above-mentioned position of the methyl groups.

2. *Pseudo-cumene* is obtained pure from brom-meta- and brom-para-xylene. The position of the methyl groups is therefore 1:3:4. It is liquid and boils at 166°. On oxidation with dilute nitric acid, xylic and paraxylic acids, $C_6H_3(CH_3)_2CO.OH$, and some xylidic acid, $C_6H_3(CH_3)(CO.OH)_2$, are produced.

Nearly all its derivatives have higher melting points than the isomeric bodies from mesitylene; e.g.

	From Mesitylene.	From Pseudo-cumene.
$C_6H_2Br(CH_3)_3$	0°	73°
$C_6H_2NO_2(CH_3)_3$	41°	71°
$C_6H_2.NH_2(CH_3)_3$	liquid	62°

By the oxidation of diamido-mesitylene hydrochloride with chromic acid, a *mesitylene hydroquinone*, $C_6HO_2(CH_3)_3$, is produced. It forms orange-coloured needles, which may be sublimed. It is moderately soluble in water and gives a fine violet coloration with alkalies.

Pseudo-cumene gives a crystalline trinitro derivative, melting at 185°. The corresponding trinitro-mesitylene melts at 232°.

1025. Other trialkyl benzenes are *ethyl-dimethyl benzene :*

$$C_6H_3(CH_3)_2C_2H_5,$$

1 : 3 : 4, boiling at 183°–184°.

Its isomer with the positions 1 : 3 : 5 boils at 180°–182°, and is obtained by the distillation of ethyl-methyl ketone with sulphuric acid.

Isoamyl-dimethyl-benzene, $C_6H_3\begin{smallmatrix}:(CH_3)_2\\ .CH_2.CH_2.CH(CH_3)_2\end{smallmatrix}$, 1 : 3 : 4, boils at 232°–233°, and *methyl-dipropyl-benzene :*

$$C_6H_3.(CH_3)(C_3H_7)_2{}^{\alpha} = (1:3:5),$$

boils at 243°–248°. It gives uvitic acid on oxidation.

Tetra-alkyl-benzenes include *durene* or tetramethyl-benzene, $C_6H_2(CH_3)_4$ (1 : 3 : 4 : 6). It is obtained by the action of sodium on monobrom-pseudo-cumene and ethylic iodide, and forms prisms melting at 80° and boiling between 189° and 191°.

A *dinitro* product, $C_6(NO_2)_2(CH_3)_4$, melting at 205°, and a *dibrom-durene,* $C_6Br_2(CH_3)_4$, melting at 199°, are known. On oxidation durene yields cumidic, $C_6H_2(CH_3)_2(CO.OH)_2$, and cumylic :

$$C_6H_2(CH_3)_3CO.OH,$$

acids.

An isomeric tetramethyl benzene, (1 : 2 : 3 : 5), from brom-mesitylene and methylic iodide, boils at 192° and does not solidify at −18°.

By the action of haloid alkyl compounds on benzene under the influence of aluminic chloride it appears possible to obtain benzenes in which all the hydrogen has been replaced by alcohol radicals.

In this way mono-, di-, &c., to hexa-ethyl benzene have been obtained and isolated.

The hexa-ethyl benzene, $C_6(C_2H_5)_6$, prepared in this manner, is said to resist all oxidising agents.

AROMATIC ALCOHOLS, $C_nH_{2n-7}.OH$.

1026. The aromatic alcohols are isomeric with the phenols, but contain the hydroxyl in combination with a side or substitution group of the benzene ring, whence the lowest number of the series is *benzyl alcohol* or *phenyl carbinol*, $C_7H_7.OH = C_6H_5.CH_2.OH$. In consequence of this constitution they are analogous in properties to the ordinary monatomic alcohols. The *primary* are oxidised to aldehydes and acids; the *secondary*, e.g. $C_6H_5.CH(OH).CH_3$, to ketones, all of which may be again reduced to the original body by nascent hydrogen (§ 160).

A convenient method of obtaining the *primary* alcohols from the aldehydes consists in the decomposition of the latter by alcoholic potash, whereby the salt of the corresponding acid is obtained along with the alcohol; e.g.

$$2C_6H_5.CHO + HOK = C_6H_5.CO.OK + C_6H_5.CH_2.OH.$$

Those primary alcohols derived from the methyl benzenes can be obtained by treatment of the hydrocarbon with chlorine or bromine at high temperatures (comp. § 1012), the resulting haloid derivative being then heated with potassic acetate, in order to convert it into the acetate, which by saponification easily yields the alcohol. Haloid acids and phosphorus chloride or bromide reconvert them into the haloid compounds, which give amine bases with ammonia and mercaptans with potassic sulphhydrate. They form unstable compounds with the alkali metals, which yield ethers with the haloid derivatives.

The hydrogen of the benzene group can also be substituted in a similar manner to the aromatic hydrocarbons themselves.

1027. *Benzylic alcohol*, $= C_6H_5.CH_2.OH$, is isomeric with cresol (§ 1015), and, as above described, may be prepared from its aldehyde, bitter almond oil, by treatment with alcoholic potash or sodium amalgam in dilute alcohol solution as well as by the action of potassic hydrate on the chloride of its radical. It occurs in nature in Peru and Tolu balsam, obtained respectively from the bark and twigs of *Myroxylon peruiferum* and *M. toluiferum*, and in storax (*Styrax liquidambar*), in which it occurs as benzoate and cinnamate. It is a colourless oily liquid, of sp. gr. 1·063 at 0°, boiling between 206° and 207°. It remains liquid at − 18°, mixes in all proportions with alcohol and ether, and oxidises first to benzoic aldehyde and finally to benzoic acid.

Heated with very strong caustic potash or with lime, a benzoate, toluene, and water are produced:

$$3C_6H_5.CH_2OH + HOK = C_6H_5.CO.OK + 2C_6H_5.CH_3 + 2OH_2.$$

Haloid benzyl compounds are obtainable from the alcohol by the action of haloid acids or phosphorus haloids. The chloride and bromide are also obtained by the direct action of the Cl and Br on toluene at its boiling point. They are isomeric with the halogen toluenes (§ 1012). Their vapours are very irritating to the eyes, &c.

Benzyl chloride, $C_6H_5.CH_2Cl$, is a colourless liquid boiling at 176°. The *bromide* boils between 201° and 202°. The *iodide*, which is obtained by the reaction of $C_6H_5.CH_2Cl$ and HI in the cold, is a crystalline body, melting at 24°, and which cannot be distilled undecomposed.

Benzylic Ethers.—Sodium alkylates react with $C_6H_5.CH_2Cl$ to form benzyl ethers, which are decomposed by chlorine gas into alkyl chloride, benzoic aldehyde, and hydrochloric acid :

$$C_6H_5.CH_2.O.C_nH_{2n+1} + Cl_2 = C_nH_{2n+1}Cl + C_6H_5.CHO + HCl.$$

Benzyl-methyl ether, $C_6H_5.CH_2.O.CH_3$, is liquid and boils at 167°–168°; *benzyl-ethyl ether* boils at 185°. Potassic phenylate also yields *benzyl-phenyl ether* with $C_6H_5.CH_2Cl$, as colourless crystals, melting at 38°–39° and boiling at 286°–287°. *Dibenzyl ether*, $C_6H_5.CH_2.O.CH_2.C_6H_5$, is obtained directly from benzyl alcohol by heating with boric anhydride:

$$2C_6H_5.CH_2.OH + B_2O_3 = 2HBO_2 + (C_6H_5.CH_2)_2O,$$

or by heating the chloride with water to 190°. It is a colourless oil boiling above 300°.

Benzyl salts are obtained by mixing the organic acid and sulphuric acid with benzyl alcohol, or by the reaction between $C_6H_5.CH_2Cl$ and the salts of the particular acids. *Benzyl acetate*, $C_6H_5.CH_2.O.C_2H_3O$, boils at 210° and possesses an odour somewhat resembling hyacinths.

The propionate, $C_3H_5O.O.CH_2.C_6H_5$, the butyrate,

$$C_4H_7O_2.CH_2.C_6H_5,$$

and the isobutyrate, $(CH_3)_2CH.CO_2.CH_2.C_6H_5$, boiling at 229°, are known.

Sulphur compounds of benzyl result from the action of benzyl chloride on the alkaline sulphides. *Benzyl mercaptan*, $C_6H_5.CH_2.SH$, is a powerfully refracting liquid, smelling like leeks and boiling at 194°–195°. *Dibenzyl sulphide*, $(C_6H_5CH_2)_2S$, crystallises in needles, melting at 49°.

Benzylamines result as halogen salts from the reaction between benzyl haloids and ammonia.

Benzylamine, $C_6H_5.CH_2.NH_2$, is a colourless liquid, miscible with water, boiling at 183°, and is isomeric with the toluidines. *Dibenzylamine*, $(C_6H_5CH_2)_2NH$, is an oily liquid, boiling at about 300°. *Tribenzylamine*, $(C_6H_5CH_2)_3N$, is a solid body crystallising in colourless plates, which melt at 91°, and is decomposed by distillation.

From benzylamine ureas, mustard oils, guanidines, and other compounds have been prepared and described; benzyl phosphines have also been obtained.

1028. *Substitution Products from Benzyl Compounds.*—By the action of chlorine on boiling parachlor-toluene or on a solution of iodine in cold benzyl chloride, *parachlor-benzyl chloride*, $C_6H_4Cl.CH_2Cl$, isomeric with the dichlor-toluenes, has been obtained as a liquid boiling at 214°. By heating with argentic acetate it yields *parachlor-benzyl acetate*, boiling point 240°, which gives by saponification *parachlor-benzyl alcohol*, $C_6H_4Cl.CH_2.OH$, a body crystallising in long needles, melting at 66°, and distilling unchanged.

By the continued action of chlorine, assisted by heating, in the presence of iodine on chlor-benzyl chloride, higher substitution products are obtained, which are nearly all liquid and can be distilled. *Pentachlor-benzyl chloride*, $C_6Cl_5.CH_2Cl$, is a solid melting at 103° and boiling at 325°. Benzyl acetate dissolves in cold fuming nitric acid, forming nitro-benzyl acetate, which is further converted by ammonia at 100° into acetamide and *nitro-benzyl alcohol* :

$$C_6H_4(NO_2).CH_2.OH,$$

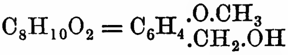
the latter substance crystallising in needles melting at 93° and very soluble in water.

Metanitro-benzyl alcohol is produced along with nitro-benzyl aldehyde by treating metanitro-benzoic acid with alcoholic potash. *Orthohydroxy-benzyl alcohol*, or *saligenin*, $C_6H_4(OH).CH_2.OH$, is obtained from its glucoside, salicin, along with grape sugar by the fermentive action of emulsin and saliva. It crystallises in pearly tables, easily soluble in alcohol, ether, and hot water, melts at 82°, and sublimes at 100°. Ferric chloride produces a deep blue colour in its solutions. Under the influence of diluted acids it is partly resinified and converted into its anhydride, the amorphous *saliretin* :

$$2C_7H_8O_2 = OH_2 + C_{14}H_{14}O_3.$$

Salicin, $C_{13}H_{18}O_7 = C_6H_7O(OH)_4O.C_6H_4CH_2OH$, occurs in the bark and leaves of most varieties of willows and several poplars. For the preparation of salicin, willow bark, reduced to small pieces, is boiled with water, the solution freed from tannin and other substances by treatment with plumbic acetate, and the lead removed by SH_2 and filtration. On evaporation the salicin crystallises from the solution in colourless prisms of bitter taste, easily soluble in water and melting at 198°. With acetic anhydride a *tetra-aceto-salicin*, $C_{13}H_4(C_2H_3O)_4O_7$, is produced, crystallising in needles.

Anisyl alcohol, para-oxymethyl-benzyl alcohol :



$$C_8H_{10}O_2 = C_6H_4\begin{array}{l}.O.CH_3\\ .CH_2.OH\end{array}$$

may also be classified with these oxy substitution products. It is obtained, together with potassic anisate, by the action of alcoholic potassic hydrate on anisic aldehyde. It crystallises in brilliant prisms, melts at 25°, and boils at 258°–259°.

Alcohols of the Formula $C_8H_{10}O$.

1029. *Tolyl alcohol*, or *paramethyl-benzyl alcohol* :

$$C_6H_4(CH_3).CH_2.OH,$$

is produced by the action of alcoholic potash on paratoluylic aldehyde. It crystallises in needles, melts at 59°, and boils at 217°. Hydrochloric acid converts it into liquid *tolyl chloride*, $C_6H_4(CH_3).CH_2Cl$.

Tolyl chloride is obtained by the action of chlorine on boiling xylene. That from coal-tar xylene mixture (§ 1021) boils between 190° and 200°.

Styronyl alcohol, or *primary phenethyl alcohol*, $C_6H_5.CH_2.CH_2.OH$, is obtained from its bromide or chloride in like manner to benzyl alcohol from the benzyl haloids; it is a liquid of 225° boiling point.

This *styronyl chloride*, $C_6H_5.CH_2.CH_2Cl$, is also produced by the action of chlorine on boiling ethyl benzene as a liquid decomposed on distillation (§ 1018).

Secondary phenethyl alcohol, $C_6H_5.CH(OH).CH_3$, is obtained by the action of sodium amalgam on aceto-phenone. Methyl-phenyl ketone, $C_6H_5.CO.CH_3$, is a pleasant-smelling oil boiling at 202°–203°.

Higher Homologues.

1030. Only a few of these bodies are known.

$C_9H_{12}O$, primary *phenyl-propyl alcohol*, $C_6H_5.CH_2.CH_2.CH_2.OH$, obtained by the saponification of liquid storax and by addition of hydrogen to cinnamic alcohol, is a thickish oil boiling at 235°. Ethyl-phenyl ketone, when treated with nascent hydrogen, yields *β-secondary phenyl-propyl alcohol*, $C_6H_5.CH(OH).CH_2.CH_3$, which boils at 210°–211°.

$C_{10}H_{14}O$, *cumin alcohol*, parapropyl or parisopropyl-benzyl alcohol, $C_6H_2(C_3H_7)CH_2OH$, is obtained by treating cuminic aldehyde with alcoholic potash as a colourless oil boiling at 243°.

Carvol, $C_{10}H_{14}O$, obtained from oil of caraway (*Carum Carvi*), and also contained in turmeric root, boils at 225°–230°, and has sp. gr. ·95.

$C_{18}H_{30}O$, *Sycoceryl Alcohol.*—This alcohol occurs as acetate in the resin of *Ficus rubiginosa*, from which it may be obtained by saponification in needles melting at 90°.

AROMATIC ALDEHYDES, KETONES, AND GLYCOLS.

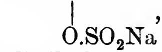
ALDEHYDES, $C_nH_{2n-7}.COH$.

Benzaldehyde, Benzoic Aldehyde, Bitter Almond Oil, $C_7H_6O = C_6H_5.COH$.

1031. This aldehyde results from the action of the ferment emulsine or synaptase on amygdalin, a glucoside (§ 74) contained in bitter almonds; it is also obtained by the oxidation of benzyl alcohol with dilute nitric acid; from heating benzylic dichloride, $C_6H_5.CHCl_2$, with water, or metallic oxides or sulphuric acid to about 50°, and by the dry distillation of a mixture of salts of benzoic and formic acids (comp. § 386):

$$(C_6H_5.CO.O)_2Ca + (HCO.O)_2Ca = 2CaCO_3 + 2C_6H_5.COH.$$

The crude product obtained by the distillation of the fermented bitter almond meal contains hydrocyanic acid, from which it may be separated by shaking with ferric chloride and milk of lime, or by addition of hydric sodic sulphite, yielding the compound



$$\begin{array}{l}C_6H_5.CH.OH\\ \quad|\\ O.SO_2Na\end{array}$$

, which is then decomposed by sodic hydrate and the oil distilled.

It is a colourless liquid boiling at 180°, of pleasant odour and high refracting power. Its sp. gr. = 1·0504 at 15°. It dissolves in thirty times its weight of water, and in alcohol and ether in all proportions.

Benzilidene dichloride, benzal chloride, $C_6H_5.CHCl_2$, isomeric with the dichlor-toluenes (§ 1012) and chlor-benzyl chloride (§ 1028), is formed by the continued action of chlorine on boiling benzyl chloride. It is a liquid boiling at 206°, giving benzaldehyde on heating with water, sulphuric acid, or metallic oxides. On heating with argentic acetate, the diacetate is formed. The corresponding bromide cannot be distilled without decomposition.

Benzilidene sulphide, $C_6H_5.CHS$, obtained by the action of benzylidene dichloride on alcoholic potassic sulphide:

$$C_6H_5.CHCl_2 + K_2S = 2KCl + C_6H_5.CHS,$$

crystallises from alcohol in colourless plates, melting between 68° and 70°, above which temperature they decompose. On treating an alcoholic solution of benzoic aldehyde with ammonic sulphide, a white amorphous body, softening at 90°–95° and insoluble in alcohol, is obtained. Analysis gives a formula C_7H_6S, but whether this substance (thio-picramil) corresponds to a polyaldehyde or to benzoïn (which see) is not settled.

Concentrated aqueous ammonia converts benzoic aldehyde into *hydrobenzamide* (§§ 424 and 939):

$$3C_6H_5.CHO + 2NH_3 = 3OH_2 + (C_6H_5.CH)_3N_2,$$

which crystallises in colourless octahedræ, insoluble in water, by long boiling with which it is slowly converted into the aldehyde and ammonia. By heating to 130° it is converted into a powerfully basic isomeric body, *amarine*, which, since it gives a diethyl compound, is perhaps $C_{21}H_{16}(NH)_2$. The same body also results when ammonia gas is passed into alcoholic benzoic aldehyde. It gives difficultly soluble monacid salts, e.g. $C_{21}H_{18}N_2.HNO_3$.

Amarine on distillation yields an isomeric compound, *lophine*, $C_{21}H_{18}N_2$, also obtainable by heating di- and tri-benzylamine. It crystallises from alcohol in needles and melts at 270°, also giving monacid salts, e.g. $2C_{21}H_{18}N_2.HCl + OH_2$.

Substitution Products from Benzoic Aldehyde.

1032. Chlorinated benzoic aldehydes are produced by heating the chlor-substitution products of benzilidene dichloride with water to a high temperature; e.g. *parachlor-benzilidene dichloride*, boiling point 234°, yields *parachlor-benzaldehyde*:

$$C_6H_4Cl_pCHCl_2 + OH_2 = 2HCl + C_6H_4Cl_p.CHO,$$

an oil distilling at 170° without decomposition. The di- and tri-chlor-aldehydes may be similarly obtained; they are solids melting at 68° and 111° respectively.

Orthochlor-benzoic aldehyde is obtained from salicylic aldehyde by the action of phosphoric chloride, the intermediate product, *orthochlor-benzilidene dichloride*, b.p. 227°–230°, being decomposed by water. It boils at 210°.

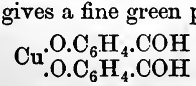
Nitro-benzoic aldehyde, $C_6H_4(NO_2)COH$, is prepared by dropping benzoic aldehyde carefully into cold fuming nitric acid; it forms colourless needles, m.p. 50°.

1033. *Salicylic aldehyde, orthohydroxy-benzaldehyde*:

$$C_6H_4(OH_o).COH,$$

occurs in different varieties of *spirea*, &c., from which it may be obtained by distillation with steam, also by the oxidation of saligenin and salicin with a mixture of potassic dichromate and sulphuric acid (3 parts salicin, 3 parts $K_2Cr_2O_7$, 36 parts OH_2, $4\frac{1}{2}$ parts SO_4H_2). It is a colourless, aromatic oil, sp. gr. 1·173, solidifying at $-20°$, boiling at 196°, slightly soluble in water.

Salicyl aldehyde combines the characters of an aldehyde with those of a phenol. It gives an intense violet coloration with iron salts, and forms compounds with strong bases, e.g. $C_6H_4(OK).COH$. An alcoholic copper solution gives a fine green precipitate of



$$Cu\begin{matrix}.O.C_6H_4.COH\\.O.C_6H_4.COH\end{matrix}$$

From these reactions it has been improperly termed an acid, as in the case of phenol. It gives crystalline compounds with alkaline sulphites, and substitution products with chlorine, bromine, and nitric acid, &c.

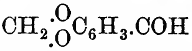
The potassic compound gives by decomposition with alkyl iodides alkyl-salicyl aldehydes; e.g.

$$KO.C_6H_4.COH + CH_3I = KI + CH_3O.C_6H_4.COH,$$

Ortho-methoxy-benzaldehyde, an oil boiling at 238°. Acetic anhydride converts the alkali compounds into *acetyl-salicyl aldehyde*, $C_2H_3O.O.C_6H_4.COH$, crystallising in fine needles, melting at 37°, boiling at 253°.

Anisic aldehyde, paramethyl oxybenzaldehyde, $CH_3.O.C_6H_4.COH$, is obtainable by warming all essential oils which contain anethol (anise, fennel, &c.) with dilute nitric acid. It is purified by means of its sodium sulphite compound and distillation with sodic hydrate. It is an exceedingly pleasant-smelling liquid, boiling at 250°, giving with alcoholic potash anisic alcohol and anisic acid.

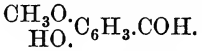
1034. *Protocatechuic aldehyde*, $C_6H_3(OH)_2COH$, is a *dihydroxybenzaldehyde*. The potassic salt of piperic acid, on distillation with twice its weight of potassic permanganate, gives *piperonal:*



$$CH_2\genfrac{}{}{0pt}{}{.O}{.O}C_6H_3.COH$$

= methen protocatechuic aldehyde, which forms colourless, pleasantly smelling crystals of m.p. 37°, b.p. 263°. Phosphoric chloride converts this body into *dichlor-piperonal dichloride*, $CCl_2\genfrac{}{}{0pt}{}{.O.}{.O.}C_6H_3.CHCl_2$, with which cold water reacts, forming hydrochloric acid and dichlor-piperonal, $CCl_2\genfrac{}{}{0pt}{}{.O.}{.O.}C_6H_3.COH$, which in turn, on heating with dilute HCl, gives protocatechuic aldehyde in flat shining needles of m.p. 150°. It is soluble in water.

Vanilline is a methyl ether of protocatechuic aldehyde:



$$\genfrac{}{}{0pt}{}{CH_3O.}{HO.}C_6H_3.COH.$$

It is often found in crystals in the vanilla bean pods, from which it may be extracted by alcohol and recrystallised from boiling water. It crystallises in long hard needles of m.p. 80°–81° and sublimes at 150°. Carbonates are decomposed by it, metallic compounds of the form $C_8H_7MO_3$ being formed. Fusing with potassic hydrate converts it into protocatechuic acid, and further to pyrocatechin.

Coniferine, $C_{16}H_{22}O_8$, a glucoside obtained from the cambium of coniferous woods, is closely related to vanilline. It crystallises in stellate groups of prisms, melting at 185°. Emulsin decomposes its aqueous solution into grape sugar and *coniferyl alcohol*, $C_{10}H_{12}O_3$, melting at 74°. This latter is apparently an ethyl derivative of vanilline, as on heating with dilute sulphuric acid and potassic dichromate it is oxidised to acetic aldehyde and vanilline.

Homologues of Benzaldehyde.

1035. *Paratoluic aldehyde*, $C_8H_8O = C_6H_4(CH_3).CHO$, is obtained by the dry distillation of a mixture of calcic paratoluate and formate, as a colourless liquid boiling at 204°.

Phenyl acetic aldehyde has been similarly obtained as a gelatinous mass.

Cumic aldehyde, or *cuminol*, $C_{10}H_{12}O = C_6H_4(C_3H_7).CHO$, occurs, together with cymene, in Roman caraway oil, from which it is separated by shaking with hydric sodic sulphite as a crystalline compound, which after washing with alcohol can be decomposed with sodic carbonate. Cumic aldehyde is a colourless oil of agreeable odour; it boils at 236°–237°, and is decomposed by alcoholic potash into cumin alcohol (§ 1030) and potassic cumate. Gentle oxidising agents convert it into cumic acid; chromic acid oxidises it to terephthalic acid.

AROMATIC KETONES,

$$C_nH_{2n-8}O = C_{n'}H_{2n'-7}.CO.C_{n''}H_{2n''+1}.$$

1036. The ketones of the above formula contain an aromatic and an alkyl nucleus united to each other by means of CO. They are prepared by the dry distillation of a mixture of the calcic salts of an aromatic and a fatty acid (comp. § 435). The group $C_{n'}H_{2n'-7}$ can evidently be united to the $CO.C_{n''}H_{2n''+1}$ group either by a carbon atom of the benzene nucleus or by the nucleus C_nH_{2n} in combination with the latter.

They unite with nascent hydrogen, yielding aromatic pinacones and secondary aromatic alcohols; on oxidation they invariably give benzoic acid.

1037. C_8H_8O. *Phenyl-methyl ketone*, or *acetophenone*:

$$C_6H_5.CO.CH_3,$$

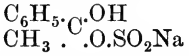
is formed by the dry distillation of a mixture of calcic benzoate and acetate:

$$(C_6H_5.CO.O)_2Ca + Ca(O.CO.CH_3)_2 = 2CaCO_3 + 2C_6H_5.CO.CH_3,$$

and by the action of benzoyl chloride on zinc dimethyl:

$$2C_6H_5.CO.Cl + Zn(CH_3)_2 = ZnCl_2 + 2C_6H_5.CO.CH_3.$$

It crystallises in large plates, melts at 14°, and boils at 200°; it gives a crystalline compound with hydric sodic sulphite:

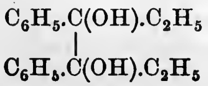


$$\begin{matrix}C_6H_5. & & .OH\\ & C & \\ CH_3\ . & & .O.SO_2Na\end{matrix}$$

Nascent hydrogen converts it into secondary phenethyl alcohol; chromic and sulphuric acids oxidise it to carbonic and benzoic acids. When heated and treated with chlorine it is converted into chlor-acetoxybenzene, $C_6H_5.CO.CH_2Cl$, a crystalline body, melting at 41° and boiling at 246°.

1038. Two isomers of the formula $C_9H_{10}O$ are known.

1. *Phenyl-ethyl ketone*, $C_6H_5.CO.C_2H_5$ (propio-phenone), is formed by the dry distillation of calcic benzoate and propionate, and by the action of benzoyl chloride on zinc ethyl. It is a colourless oil, boiling at 208°–210°, which does not combine with alkaline hydric sulphites. Chromic acid oxidises it to benzoic and acetic acids, and by treatment of its aqueous alcoholic solution with sodium amalgam secondary phenylpropyl alcohol is formed, and in addition a pinacone:



$$\begin{matrix}C_6H_5.C(OH).C_2H_5\\ |\\ C_6H_5.C(OH).C_2H_5\end{matrix}$$

which crystallises from alcoholic solution in spear-shaped crystals, melting at 120°.

2. *Benzyl-methyl ketone*, $C_6H_5.CH_2.CO.CH_3$, obtained from calcic acetate and phenyl acetate, is liquid, boils at 214°–216°, unites with hydric sodic sulphite, and yields benzoic and acetic acids on oxidation.

1039. Four isomers of the formula $C_{10}H_{12}O$ have been prepared.

1. *Phenyl-propyl ketone*, $C_6H_5.CO.C_3H_7$, is obtained as an oil, boiling at 220°–222°, on the dry distillation of calcic benzoate and butyrate; on oxidation it yields benzoic and propionic acids.

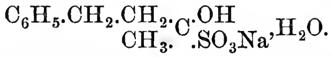
2. *Phenyl-isopropyl ketone*, $C_6H_5.CO.CH(CH_3)_2$, prepared by distillation of calcic benzoate and isobutyrate, boils below 217° and gives benzoic, acetic, and carbonic acids on oxidation.

3. *Benzyl-ethyl ketone*, $C_6H_5.CH_2.CO.C_2H_5$, obtained by action of phenyl-chloracetyl on zinc diethyl, boils at 225°–226°, and gives benzoic and propionic acids when oxidised.

4. *Phenethyl-methyl ketone*, $C_6H_5.CH_2.CH_2.CO.CH_3$. Ethylic sodaceto-acetate (§ 786), when treated with benzylic chloride, is converted into ethylic benzyl aceto-acetate:

$$\begin{matrix}CH_3\,.\,CO\\C_6H_5.CH_2.\end{matrix}CH.CO.O.C_2H_5,$$

which on saponification gives alcohol, a carbonate, and phenethyl-methyl ketone. This latter is an oil boiling at 235°–236°, and giving a crystalline compound with hydric sodic sulphite:



$$\begin{matrix}C_6H_5.CH_2.CH_2.\\CH_3.\end{matrix}C\begin{matrix}.OH\\.SO_3Na\end{matrix},H_2O.$$

Chromic acid oxidises it to benzoic, carbonic, and acetic acids.

1040. *Phenyl-isobutyl ketone:*

$$C_{11}H_{14}O = C_6H_5.CO.CH_2.CH(CH_3)_2,$$

is obtained by the dry distillation of calcic benzoate and isovalerate; it boils at 225°–226°, and yields benzoic and isobutyric acids on oxidation.

AROMATIC GLYCOLS.

1041. Only a single true aromatic glycol has yet been obtained with certainty.

Tollylene glycol, *xylene glycol*, or *paraphenylene dicarbinol*, $C_8H_{10}O_2 = C_6H_4(CH_2.OH)_2$. Paraxylene, when treated with chlorine gas at 140°, gives *tollylene dichloride*, $C_6H_4(CH_2Cl)_2$, melting at 100°, or with bromine yields *tollylene dibromide*, $C_6H_4(CH_2Br)_2$, in plates melting at 145°–147°. When these haloids are heated at 180° with 30 times their weight of water, they are converted into the glycol *tollylene dihydrate*, $C_6H_4(CH_2.OH)_2$, which crystallises in needles melting at 112°–113°, and is readily soluble in water. *Tollylene diiodide*, $C_6H_4(CH_2I)_2$, obtained by heating the glycol with hydriodic acid, forms fine needles, melting at 170° with decomposition and readily soluble in chloroform.

The halogen compounds react with potassic acetate at 140°, forming *tollylene diacetate*, crystalline plates, and when treated with alcoholic potassic hydrate give the *monethyl ether* of tollylene glycol,

$C_6H_4\begin{matrix}.CH_2.O.C_2H_5\\.CH_2.OH\end{matrix}$, in the form of an oil of agreeable odour, boiling at 252°. Chromic acid oxidises tollylene glycol to terephthalic acid.

Phenyl Alkylenes.

1042. *Styrolene, cinnamene,* or *phenyl ethylene:*

$$C_8H_8 = C_6H_5.CH:CH_2,$$

is a constituent of liquid storax, from which it can be obtained by distillation with water as a thin oil, boiling at 145° and of sp. gr. ·924°. It can be prepared by heating cinnamic acid with lime:

$$C_6H_5.CH:CH.CO.OH + CaO = CaCO_3 + C_6H_5.CH:CH_2;$$

by boiling phenethyl chloride (§ 1029) with alcoholic potassic hydrate:

$$C_6H_5.CH_2.CH_2.Cl + KOH = KCl + H_2O + C_6H_5.CH:CH_2;$$

and, together with benzene, by the action of a red heat on acetylene. On long standing, or more quickly at 200°, it polymerises to an amorphous, transparent solid, *metastyrolene,* which is again converted into styrolene on distillation.

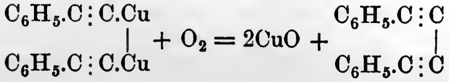
It unites directly with the halogens, forming styrolene dihaloids. *Styrolene dichloride,* $C_8H_8Cl_2 = C_6H_5.CHCl.CH_2Cl$, is liquid; the *dibromide,* $C_8H_8Br_2$, crystallises in plates and needles melting at 68°–69°. They both decompose on heating, either alone or with strong bases, into *α-chlor-styrolene,* $C_6H_5.CH:CHCl$, and *α-brom-styrolene,* $C_6H_5.CH:CHBr$, liquids which cannot be distilled unaltered. The isomeric β-halogen styrolenes are formed by the dry distillation of phenyl-chlor- and phenyl-brom-lactic acids (§ 1096). *β-Chlor-styrolene,* $C_6H_5.CCl:CH_2$, is an oil boiling at 199°, of hyacinth-like odour; *β-brom-styrolene,* $C_6H_5.CBr:CH_2$, boils at 228°. *Styrolene diiodide,* $C_8H_8I_2$, is formed by mixing styrolene with solution of iodine in potassic iodide; it cannot be preserved, as it decomposes readily into iodine and metastyrolene.

On heating styrolene dibromide or α-brom-styrolene with alcoholic potassic hydrate at 120°

Phenyl acetylene, or *acetenyl benzene,* $C_8H_6 = C_6H_5.C\vdots CH$ (comp. § 759), is obtained as a colourless oil boiling at 140°.

Like acetylene, allylene, &c., it can exchange the hydrogen atom of the $\vdots C.H$ group for metal; with ammoniacal cuprous chloride it gives a yellow precipitate, $(C_8H_5)_2Cu_2$; with ammoniacal silver solutions, a white precipitate of $\begin{matrix}C_6H_5.C\vdots C.Ag.Ag.\\C_6H_5.C\vdots C.Ag.Ag.\end{matrix}O$; with metallic sodium hydrogen is evolved, and a white substance, *sodium phenyl acetylene,* $C_6H_5.C\vdots CNa$, produced, which is spontaneously inflammable in air.

The silver and copper compounds give phenyl acetylene when treated with hydrochloric acid. On shaking the copper compound with air in presence of alcoholic ammonia, *diacetenyl phenyl,* $C_{16}H_{10}$, is formed:



$$\begin{array}{c}C_6H_5.C\vdots C.Cu\\ \qquad\quad|\\ C_6H_5.C\vdots C.Cu\end{array} + O_2 = 2CuO + \begin{array}{c}C_6H_5.C\vdots C\\ \qquad\quad|\\ C_6H_5.C\vdots C\end{array}$$

This latter crystallises in long brittle needles, melting at 97° and insoluble in water.

1043. *Homologues of Styrolene.—a-Phenyl propylene*

$$C_9H_{10} = C_6H_5.CH : CH.CH_3,$$

is formed in small quantity, together with phenyl-propyl alcohol, by treatment of cinnamic alcohol with sodium amalgam.

It is a colourless oil, boiling between 165° and 170°, and unites with bromine to form a crystalline dibromide, $C_9H_{10}Br_2$, crystallising at 66·5°.

β-Phenyl propylene, or *allyl benzene:*

$$C_9H_{10} = C_6H_5.CH_2.CH:CH_2,$$

is obtained by heating allylic bromide with benzene and zinc dust. It is a liquid boiling at 155°.

Phenyl butylene, $C_{10}H_{12}$, can be prepared synthetically by the action of sodium on benzylic chloride and allylic iodide:

$$\begin{aligned} C_6H_5.CH_2Cl + I.CH_2.CH:CH_2 + Na_2 &= NaCl + NaI \\ &+ C_6H_5.CH_2.CH_2.CH:CH_2. \end{aligned}$$

It is a colourless oil, boiling between 176° and 178° and giving a liquid dibromide.

AROMATIC ACIDS, $C_nH_{2n-8}O_2 = C_{n'}H_{2n'-7}.CO.OH$, AND THEIR SUBSTITUTION PRODUCTS.

1044. The aromatic acids of the formula $C_nH_{2n-8}O_2$ fall naturally into two chief groups.

1. *Aromatic acids* proper, in which the CO.OH group is directly united to the carbon of the benzene nucleus.

These comprise the first member of the series, *benzoic acid :*

$$C_7H_6O_2 = C_6H_5.CO.OH,$$

and its alkyl substitution products :

$$C_6H_4\left\{\begin{array}{l}C_nH_{2n+1}\\CO.OH\end{array}\right., \quad C_6H_3\left\{\begin{array}{l}(C_nH_{2n+1})_2\\CO.OH\end{array}\right., \text{ \&c.}$$

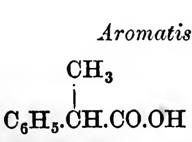
2. *Aromatised fatty acids,* in which a hydrocarbon group, C_nH_{2n}, is placed between the benzene nucleus and the CO.OH group. They may be regarded as derivatives of the fatty acids, $C_nH_{2n+1}.CO.OH$, in whose alkyl group a hydrogen atom has been replaced by a benzene nucleus. This latter can either be phenyl or an alkyl-substituted phenyl. In these ways the number of possible isomers becomes very large, as shown by the following list of acids of the formula $C_9H_{10}O_2$:—

Aromatic Acids.

$C_6H_4\left\{\begin{array}{l}C_2H_5\\CO.OH\end{array}\right.$ ethyl benzoic acid, 3 varieties, o., p., m.

$C_6H_3\left\{\begin{array}{l}(CH_3)_2\\CO.OH\end{array}\right.$ dimethyl benzoic acid, 6 varieties.

Aromatised Fatty Acids.



$$C_6H_5.\overset{\overset{\displaystyle CH_3}{|}}{C}H.CO.OH$$

α-phenyl propionic acid.

$C_6H_5.CH_2.CH_2.CO.OH$, β-phenyl propionic acid.

$C_6H_4\left\{\begin{array}{l}CH_3\\CH_2.CO.OH\end{array}\right.$ methyl-phenyl acetic acid, 3 varieties, o., p., and m.

The hydrocarbon groups united to CO.OH can have their hydrogen substituted for other elements or radicals, whilst the acid group CO.OH is capable of all those metamorphoses previously mentioned (comp. § 535), yielding salts, acid anhydrides, halogen and nitrogen derivatives, &c.

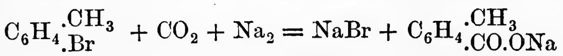
1045. *Formation of Aromatic Acids.*—In addition to the oxydation of the corresponding aldehydes, alcohols, and alkylised benzenes (§ 1009), the aromatic acids can be formed by a series of synthetic processes, which, for the aromatised fatty acids, completely agree with those for the synthesis of the fatty acids themselves (comp. § 559), and are somewhat similar for benzoic acid and its alkyl substitutes, though somewhat modified by the nature of the benzene nucleus. The most important of them may be classified as follows, according to the materials employed as starting points:—

1. The *halogen substitution products* of the aromatic hydrocarbons, especially the bromine compounds, yield—

a. Alkyl salts, when mixed with alkyl chloro-carbonates, treated with sodium amalgam, and gently heated; e.g.

$$C_6H_5Br + Cl.CO.O.C_2H_5 + Na_2 = NaBr + NaCl$$
$$+ C_6H_5.CO.O.C_2H_5.$$

b. Sodic salts of aromatic acids when carbonic anhydride is led into their ethereal solutions, which are at the same time treated with sodium; e.g.



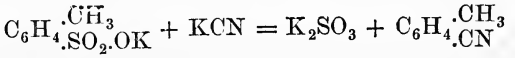
$$C_6H_4\begin{matrix}.CH_3\\.Br\end{matrix} + CO_2 + Na_2 = NaBr + C_6H_4\begin{matrix}.CH_3\\.CO.ONa\end{matrix}$$

2. The *aromatic sulphonic acids* exchange the group $SO_2.OH$ for $CO.OH$—

a. By heating their alkaline salts with alkaline formates; e.g.

$$C_6H_5.SO_2OK + KO.CHO = K_2SO_3 + C_6H_5.CO.OH.$$

b. By dry distillation with potassic cyanide, when aromatic cyanides (the nitriles of the acids) are first formed; e.g.



$$C_6H_4\begin{matrix}.CH_3\\.SO_2.OK\end{matrix} + KCN = K_2SO_3 + C_6H_4\begin{matrix}.CH_3\\.CN\end{matrix}$$

which, like all true cyanides, are converted by bases or acids in the presence of water into ammonia and aromatic acids (comp. § 558, 3).

3. These same nitriles are formed by long heating of aromatic isocyanides to temperatures of 200° and above:

$$C_6H_5.N \vdots C = C_6H_5.C \vdots N,$$

and by desulphurising the isosulpho-cyanates by heating with powdered copper:

$$C_6H_5.N:C:S + Cu_2 = Cu_2S + C_6H_5.C \vdots N.$$

1046. By dry distillation of a mixture of the salt of an aromatic acid with a strong base, the CO.OH group is exchanged for hydrogen, and a hydrocarbon containing one atom of carbon less is obtained. This process occurs most readily when calcic salts are heated with calcic hydrate; e.g.

$$(C_6H_5.CO.O)Ca + Ca(OH)_2 = 2CaCO_3 + 2C_6H_6$$
$$[C_6H_3(CH_3)_2CO.O]_2Ca + Ca(OH)_2 = 2CaCO_3 + 2C_6H_4(CH_3)_2.$$

Dry distillation of the calcic salts with calcic formate converts them into the corresponding aldehydes (§ 386), which can be further converted into the primary alcohols.

BENZOIC ACID, $C_7H_6O_2 = C_6H_5.CO.OH$.

1047. Benzoic acid occurs in several resins, either free or in the form of ethereal salts (e.g. in gum benzoïn, from *Styrax Benzoïn*), and at times it occurs naturally in the urine of herbivorous animals.

It is obtained synthetically by the oxidation of benzoic aldehyde, the monalkyl benzenes (§ 1009)—for instance, toluene—and the whole of the aromatised fatty acids with non-substituted phenyl groups:

$$C_6H_5.C_nH_{2n}.CO.OH + 3nO = nCO_2 + nH_2O + C_6H_5.CO.OH.$$

It can be prepared, by the general methods already given, from brom-benzene, benzene-monosulphonic acid, and phenyl isosulphocyanide. It is obtained in small quantity by the oxidation of albuminoids or of benzene, either alone or mixed with formic or oxalic acids. The chief source of the benzoic acid occurring in commerce is hippuric acid, or benzoyl-glycocine, a substance occurring in the urine of herbivorous Mammalia; on boiling with acids or alkalies, or by putrid fermentation, this is resolved into glycocine and benzoic acid or their respective salts (comp. § 717).

It is best obtained from gum benzoïn by slow heating in a flat iron pan lightly covered with filter paper and having a paper hood. The vapours of the acid pass through the filter paper and condense on the paper hood in needles. It is purified by recrystallisation from boiling water, resublimation or distillation with water.

Benzoic acid crystallises in shining, colourless, flexible, flattened needles or leafy crystals, melting at 120° and volatilising with water vapour below 100°; it boils at 250°. At ordinary temperatures it has a pleasant aromatic odour, but when its vapour is more freely evolved it produces coughing. It dissolves in about 200 parts of cold and 24 parts of boiling water, in two parts cold and 1 part boiling absolute alcohol, and readily also in ether, benzene, and oils.

By action of sodium amalgam on an aqueous solution of benzoic acid this is partly reduced to benzylic alcohol, whilst at the same time, together with other bodies, a *hydrogen addition product, benzoleïc acid*, $C_7H_{10}O_2 = C_6H_9.CO.OH$, is formed, as an oil which is oxidised by atmospheric oxygen, again yielding benzoic acid.

1048. The *salts* of benzoic acid, the *benzoates*, are mostly readily soluble in water and crystallisable. Their dilute aqueous solutions give with ferric chloride an amorphous reddish brown precipitate of basic ferric benzoate. The alkali salts are very readily soluble in water. $C_7H_5KO_2,3H_2O$ and $C_7H_5NaO_2,H_2O$ crystallise in needles, frequently united to tufts; $(C_7H_5O_2)_2Ba,3H_2O$ and

$$(C_7H_5O_2)_2Ca,2H_2O$$

are also readily soluble; $(C_7H_5O_2)_2Pb,H_2O$ and $C_7H_5AgO_2$ are crystalline powders, difficultly soluble in cold water.

The ethereal salts of benzoic acid are obtained similarly to those of the fatty acids. *Methylic benzoate*, $C_6H_5.CO.O.CH_3$, boiling at 199°, and *ethylic benzoate*, boiling at 211°, are colourless liquids, heavier than water, of agreeable odour. *Benzylic benzoate*:

$$C_6H_5.CO.O.CH_2.C_6H_5,$$

occurs largely in the liquid portion of Peru balsam: on cooling it crystallises in plates, melts at about 20°, and boils above 300°.

Populine, $C_{20}H_{22}O_8,2H_2O$, or *benzoyl salicine*, occurs in the bark and leaves of the aspen (*Populus tremula*), and is prepared similarly to salicine. It is obtained artificially by melting salicine with benzoic anhydride; it crystallises in small prisms of sweet taste, and decomposes into salicine and benzoic acid on boiling with baryta water, and into sugar, saligenin, and benzoic acid with mineral acids.

1049. *Chlor-benzoyl*, $C_6H_5.CO.Cl$, is prepared by the action of phosphoric chloride on benzoic acid or of chlorine on benzoic aldehyde:

$$C_6H_5.CO.H + Cl_2 = HCl + C_6H_5.CO.Cl.$$

It is a liquid of unpleasant burning taste, which boils at 199° and is slowly decomposed by water into benzoic and hydrochloric acids. By heating with potassic bromide or iodide, brom-benzoyl and iod-benzoyl are respectively obtained. By the action of phosphoric chloride at 180° *benzo-trichloride*, $C_6H_5.CCl_3$, is obtained as a liquid boiling at 213°–214; this is also formed by the long-continued action of chlorine on toluene at the boiling temperature.

1050. *Benzoic anhydride*, $C_{14}H_{10}O_3 = (C_6H_5.CO)_2O$, is obtained by the action of benzoyl chloride on sodic benzoate or by the decomposition of six parts of the latter salt with one part of phosphoric oxychloride (comp. § 633). The sodic salts formed are dissolved in water and the residual anhydride crystallised from alcohol. It forms oblique prisms, and is only slowly converted into benzoic acid on boiling with water; it melts at 42° and boils at 310°.

Mixed anhydrides of the benzoic acid radical with those of the fatty acid are formed by treating the chloride of one acid radical with the sodic salt of the other:

$$C_6H_5.CO.Cl + NaO.CO.CH_3 = NaCl + C_6H_5.CO.O.CO.CH_3$$
$$C_6H_5.CO.ONa + Cl.CO.CH_3 = NaCl + C_6H_5.CO.O.CO.CH_3.$$

They are not volatile as such, being resolved on distillation into simple anhydrides containing like acid radicals. For instance, on heating *aceto-benzoic anhydride* to 150° acetic anhydride distils, whilst benzoic anhydride remains behind:

$$2C_6H_5.CO.O.CO.CH_3 = (C_6H_5.CO)_2O + (CH_3.CO)_2O.$$

1051. *Benzamide*, $C_7H_7ON = C_6H_5.CO.NH_2$, is formed by the decomposition of ethereal salts of benzoic acid, benzoic anhydride, and chlor-benzoyl with ammonia (comp. § 636). It crystallises in shining plates and tables, melts at 125°, and distils at about 290°. It is moderately soluble in boiling water, more readily in alcohol and ether. Chlor-benzoyl, when treated with aniline, yields *phenyl benzamide*, $C_6H_5.CO.N(C_6H_5)H$, and *phenyl dibenzamide*:

$$(C_6H_5.CO)_2:N.C_6H_5,$$

both in the form of difficultly soluble crystalline compounds.

Benzoyl glycocine, or hippuric acid:

$$C_9H_9NO_3 = HO.CO.CH_2.N(CO.C_6H_5)H,$$

occurs in the urine of herbivorous animals, and in very small quantity in human urine, the amount in the latter being largely increased when benzoic acid, toluene, benzoic aldehyde, cinnamic or quinic acids are taken internally. It can be obtained artificially by the action of benzoyl chloride on argento-glycocine (§ 719):

$$HO.CO.CH_2.NAgH + Cl.CO.C_6H_5 = AgCl \\ + HO.CO.CH_2.N(CO.C_6H_5)H,$$

and by heating benzamide with chlor-acetic acid. It is prepared from the urine of cows and horses, by evaporating to a fourth of the original volume and then acidulating with hydrochloric acid; the separated crude acid is then crystallised from boiling water to which a little chlorine water has been added. It forms shining rhombic prisms, soluble in 600 parts of cold water. It yields salts with metals, but on long boiling with bases or acids splits up into benzoic acid and glycocine.

On heating with plumbic oxide it is converted into benzamide, the glycocine residue being oxidised; with nitrous acid it yields benzo-glycollic acid:

$$HO.CO.CH_2.N(CO.C_6H_5)H + HONO = N_2 + H_2O \\ + HO.CO.CH_2.O(CO.C_6H_5).$$

Benzo-nitrile, or *phenyl cyanide*, $C_7H_5N = C_6H_5.CN$, is formed, in addition to the methods already given at § 1045, 2 and 3, by the distillation of ammonic benzoate or benzamide with phosphoric anhydride (comp. § 636) and by heating chlor-benzoyl with potassic sulphocyanate:

$$2C_6H_5.CO.Cl + 2KS.CN = 2KCl + CO_2 + CS_2 + 2C_6H_5.CN.$$

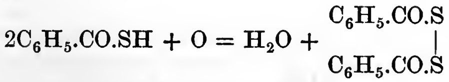
It is a colourless oil, boiling at 191°, of sp. gr. 1·023 at 0°, which is converted into benzoic acid and ammonia by aqueous acids or alkalies, and combines with four atoms of nascent hydrogen, forming benzylamine (comp. § 266).

1052. *Sulphur Compounds.*—Chlor-benzoyl, when treated with an alcoholic solution of potassic sulphide, yields the potassic salt of *thiobenzoic acid:*

$$C_6H_5.CO.Cl + KSK = KCl + C_6H_5.CO.SK,$$

from which hydrochloric acid liberates the free acid as a fibro-crystalline mass nearly insoluble in water.

It cannot be volatilised alone, but distils with water vapour. Its ethereal solution oxidises in air to *benzoyl persulphide:*



$$2C_6H_5.CO.SH + O = H_2O + \begin{array}{c} C_6H_5.CO.S \\ | \\ C_6H_5.CO.S \end{array}$$

Benzo-trichloride (§ 1049) reacts with potassic sulphide in alcoholic solution, forming potassic dithio-benzoate:

$$C_6H_5.CCl_3 + 2K_2S = 3KCl + C_6H_5.CS.SK,$$

from which *dithio-benzoic acid*, $C_6H_5.CS.SH$, can be separated as an unstable violet-red oil.

Substitution Products of Benzoic Acid.

1053. Three isomeric groups of mono-substitution products can be derived from benzoic acid in which a hydrogen atom of the benzene nucleus has been replaced by halogens, nitro or amido groups, hydroxyl, &c., whose metamorphoses correspond in all essentials with those of the benzene substitution products.

By the direct action of halogens, nitric acid, and sulphuric anhydride on benzoic acid, derivatives of the meta group are formed either principally or exclusively, all of which can be converted into metahydroxy-benzoic acid. The same bodies are obtained by the oxidation of the meta-substitution products of toluene. Similarly para-substitution products of toluene yield para-substituted benzoic acids, whilst, on the other hand, the ortho-substituted toluenes are generally completely destroyed on oxidation.

The most important materials for the preparation of ortho-substituted benzoic acids are ortho-hydroxy-benzoic or salicylic acid and ortho-nitro-benzoic acid, the latter being obtained in not inconsiderable quantity together with metanitro-benzoic acid by the nitration of benzoic acid.

1054. The *halogen benzoic acids* are solid sublimable compounds, difficultly soluble in water. The ortho and meta derivatives crystallise in needles, the para compounds in leafy plates. On dry distillation with lime they yield halogen benzenes; e.g.

$$C_6H_4Cl.CO.OH + Ca(OH)_2 = CaCO_3 + H_2O + C_6H_5Cl.$$

Chlor-benzoic Acids, $C_6H_4Cl.CO.OH$.—*Orthochlor-benzoic acid,* or *chlor-salylic acid,* is obtained from salicylic acid by the action of phosphoric chloride:

$$C_6H_4(OH).CO.OH + 2PCl_5 = 2POCl_3 + 2HCl + C_6H_4Cl.CO.Cl,$$

and decomposition of the resulting *orthochlor-benzoyl chloride* (an oil boiling at 240°) with water:

$$C_6H_4Cl.CO.Cl + H_2O = HCl + C_6H_4Cl.CO.OH.$$

It crystallises in colourless needles, melting at 137° when dry, but below 100° when moist; it is more readily soluble in water than its isomers.

Metachlor-benzoic acid is formed by the oxidation of metachlortoluene and by the chlorination of benzene by nascent chlorine (from potassic chlorate and hydrochloric acid, or from antimonic chloride on heating); it crystallises in needles melting at 152°. *Parachlor-benzoic acid,* or *chlor-dracylic acid,* obtained by the oxidation of parachlor-toluene, melts at 234° and sublimes in brilliant scales.

Brom-benzoic Acids, $C_6H_4Br.CO.OH$.—The ortho acid is prepared from ortho-diazo-benzoic acid by heating with bromine and alcohol. The isomers are prepared from the corresponding chlor-benzoic acids. They are characterised by their melting points:

137°–138°	155°	250°
Ortho-	Meta-	Para-brom-benzoic acid.

Iodo-benzoic acids, $C_6H_4I.CO.OH$, are prepared from the corresponding diazo-benzoic acid sulphates by heating with hydriodic acid (comp. § 976), the para acid also by oxidation of paraiodo-toluene; they have the following melting points:

159° (ortho). 185°–187° (meta). 267° (para).

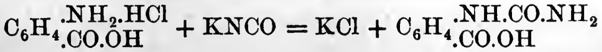
1055. *Nitro-benzoic Acids*, $C_6H_4(NO_2).CO.OH$.—One part of fused and powdered benzoic acid is intimately mixed, two parts of potassic nitrate and three parts of sulphuric acid then added; on treatment of the mass with water a mixture of nitro-benzoic acids is left, consisting principally of the meta acid together with smaller quantities of the ortho acid and a trace of paranitro-benzoic acid. They are best separated in the form of their baric salts, that of the ortho acid being more readily soluble than baric metanitro-benzoate. The para acid is most readily obtained by the oxidation of solid nitro-toluene:

	Ortho.	Meta.	Para.
Melting point	145°	141°–142°	238°
Crystalline form	Prisms.	Needles and plates.	Plates.
Amount of water at 16·5° required to dissolve 1 part of acid	164 parts.	425 parts.	Still more.

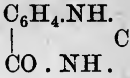
1056. *Amido-benzoic acids*, $C_6H_4(NH_2).CO.OH$, are obtained by reduction of the nitro-benzoic acids with ammonic sulphide or with tin and hydrochloric acid. On employment of the latter method the resulting dilute solution is supersaturated with sodic carbonate, filtered from the precipitated basic zinc carbonate, the filtrate concentrated, and excess of acetic acid added, when the amido-benzoic acids crystallise out. Orthamido-benzoic acid, or *anthranilic acid*, is formed from indigo by long boiling with solution of sodic hydrate and continued addition of manganic oxide; the clear yellow solution is then neutralised with sulphuric acid, evaporated to dryness, and extracted with alcohol. This latter dissolves sodic orthamido-benzoate, which is finally decomposed by acetic acid The amido-benzoic acids melt at 144° (ortho), 173°–174° (meta), 186°–187° (para).

They crystallise in needles, dissolve in hot water and alcohol, and possess an acid reaction. Like glycocine and its homologues, they yield salts with acids and bases, and as aromatic amines show similar changes to aniline; e.g. meta-amido-benzoic acid, on heating with glacial acetic acid, is converted into *acetmet-amido-benzoic acid*, $C_6H_4(N.C_2H_3O.H).CO.OH$, metameric with hippuric acid (§ 1051); it forms a microcrystalline powder, melting at 220°–230°, difficultly soluble in water and converted into metamido-benzoic acid hydrochloride, $C_6H_4(NH_3Cl).CO.OH$, and acetic acid by heating at 140° with hydrochloric acid. Ethyl and diethyl meta-amido-benzoic acid, $C_6H_4(N.C_2H_5.H).CO.OH$ and $C_6H_4(N[C_2H_5]_2).CO.OH$, are also known.

Amido-benzoic acid hydrochlorides react in aqueous solution with potassic pseudo-cyanate, forming uramido-benzoic acids (comp. hydantoïc acid, § 724):



$$C_6H_4\genfrac{}{}{0pt}{}{.NH_2.HCl}{.CO.OH} + KNCO = KCl + C_6H_4\genfrac{}{}{0pt}{}{.NH.CO.NH_2}{.CO.OH}$$

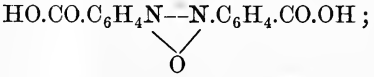
The meta compound crystallises in colourless needles with one molecule of water of crystallisation, and evolves water at 200°, being converted into a urea derivative,  $\begin{matrix}C_6H_4.NH.\\ | \\ CO\,.\,NH.\end{matrix}\!\!>CO$ CO, corresponding to hydantoïn.

1057. By the action of nitrous acid on nitric acid solutions of the amido-benzoic acids, *diazobenzoic acid nitrates*, $C_6H_4\begin{smallmatrix}.N_2.O.NO_2\\ .CO.OH\end{smallmatrix}$, separate, which behave similarly to diazo-benzene nitrate (§ 977), explode on heating, are converted into nitrogen, nitric acid, and hydroxy-benzoic acids on heating with water, and on treatment with halogen hydro-acids yield halogen-substituted benzoic acids.

By passing nitrous anhydride into alcoholic solutions of the amido-benzoic acids orange yellow granules of diazo-amido-benzoic acids are obtained; these are also obtained directly by mixing amido-benzoic acids with diazo-benzoic acid nitrates (comp. § 978). They are nearly insoluble in water, alcohol, and ether, and are weak dibasic acids, which explode when heated alone. Halogen hydro-acids decompose them as shown in the following equation:

$$C_6H_4\begin{smallmatrix}.(N_2).NH.C_6H_4.CO.OH\\ .CO.OH\end{smallmatrix} + 2HCl = C_6H_4\begin{smallmatrix}.Cl\\ .CO.OH\end{smallmatrix}$$
$$+ (NH_3.Cl).C_6H_4.CO.OH + N_2.$$

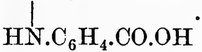
1058. The nitro-benzoic acids, on boiling in alcoholic solution with potassic hydrate, yield *azoxy-benzoic acids:*



$$HO.CO.C_6H_4N\!-\!\!-\!N.C_6H_4.CO.OH\,;\quad \text{(N–N bridged by O)}$$

whilst when treated with sodium amalgam they give *azobenzoic acids:*

$$HO.CO.C_6H_4.N{=}N.C_6H_4.CO.OH\,;$$

and these finally, on boiling with ferrous salts and sodic hydrate, yield *hydrazo-benzoic acids*,  $\begin{matrix}HN.C_6H_4.CO.OH\\ | \\ HN.C_6H_4.CO.OH\end{matrix}$. The latter are weak, the former strong, dibasic acids (comp. § 975).

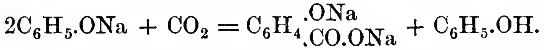
1059. *Sulpho-benzoic acids*, $C_6H_4\begin{smallmatrix}.SO_2.OH\\ .CO.OH\end{smallmatrix}$, are formed by heating benzoic acid with Nordhausen sulphuric acid, and by passing the vapours of sulphuric anhydride over dry benzoic acid. The product is diluted with water neutralised with baric carbonate, and on evaporation the difficultly soluble baric salt of the *para* compound first separates, whilst later the more readily soluble *meta* compound, $C_6H_4\begin{smallmatrix}.CO.O\\ .SO_2.O\end{smallmatrix}Ba$, is obtained, this latter being formed in by far the largest quantity. From these salts the free acids can be obtained as strongly acid crystalline masses, both readily soluble in water. The meta acid deliquesces in air; its acid baric salt, $\left(C_6H_4\begin{smallmatrix}.SO_2.O\\ .CO.OH\end{smallmatrix}\right)_2Ba$, is difficultly soluble, that of the para acid nearly insoluble in water.

Hydroxy-benzoic Acids, $C_6H_4(OH)CO.OH$.

1060. The *hydroxy-benzoic acids* combine the properties of acids with those of phenols, and may therefore be designated as *phenol benzoic acids.* They yield monobasic salts when treated with alkaline carbonates, but with the hydrates of the strongly basic metals they also exchange the phenol-hydroxyl hydrogen atom for metal. All three acids yield phenol when heated with lime :

$$C_6H_4(OH).CO.OH + Ca(OH)_2 = CaCO_3 + H_2O + C_6H_5.OH.$$

1061. *Ortho-hydroxy-benzoic acid*, or *salicylic acid*, occurs in the flowers of Spiræa, and as its methylic salt forms the chief constituent of the American winter green oil (from *Gaultheria procumbens*). It is obtained synthetically from phenol by the simultaneous action of sodium and carbonic anhydride; most conveniently by heating sodium phenol at 180° in a stream of carbonic anhydride, when one-half of the phenol distils, leaving a residue of dibasic sodic salicylate :



$$2C_6H_5.ONa + CO_2 = C_6H_4\begin{matrix}.ONa\\ .CO.ONa\end{matrix} + C_6H_5.OH.$$

It is also formed by the oxidation of saligenin (§ 1028) and salicylic aldehyde (§ 1033), or by fusion of ortho-halogen benzoic acids, potassic ortho-toluene sulphonate, or ortho-cresol (§ 1015) with caustic potash.

Salicylic acid crystallises in colourless tetragonal prisms, melting at 156° and dissolving readily in alcohol, ether, and boiling water (15–20 parts), but requiring nearly 2,000 times its weight of cold water for solution. At 220° it decomposes into phenol and carbonic anhydride, but can be sublimed unaltered on careful heating. Its normal sodic salt decomposes at 220° into dibasic sodic salicylate, phenol, and carbonic anhydride :

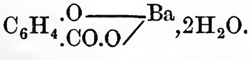
$$2C_6H_4\begin{matrix}.OH\\ .CO.ONa\end{matrix} = C_6H_4\begin{matrix}.ONa\\ .CO.ONa\end{matrix} + C_6H_5.OH + CO_2.$$

The potassic salt suffers an analogous change, but the residue consists not of salicylate but of dibasic potassic paroxy-benzoate.

Like phenol, salicylic acid gives a deep bluish-violet coloration with ferric chloride. The alkali salts are all pretty readily soluble and crystallisable. Normal *baric salicylate :*

$$[C_6H_4(OH).CO.O]_2Ba,H_2O,$$

forms needles, and on addition of baryta water to its boiling aqueous solution gives difficultly soluble plates of the dibasic salt :

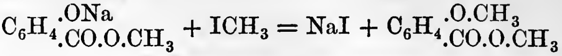


$$C_6H_4\begin{matrix}.O\text{———}\\ .CO.O\diagup\end{matrix}Ba,2H_2O.$$

The ethereal salts of salicylic acid can be readily obtained by heating salicylic acid with sulphuric acid and the respective alcohols. On mixing them with cold concentrated solutions of alkalies, metallic derivatives separate, $C_6H_4(OM).CO.O.C_nH_{2n+1}$, in crystalline form, and yield the ethereal salt again on addition of acids, but salts of salicylic acid and alcohol on boiling with water. *Methylic salicylate*,

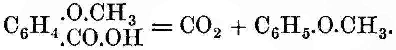
$C_6H_4(OH).CO.O.CH_3$, occurring naturally in gaultheria oil, is a colourless oil of pleasant aromatic odour, boiling at 224°; the *ethylic salt* boils at 221°. Both are heavier than water, are difficultly soluble therein, and give violet colours with ferric chloride.

1062. On heating the above-mentioned metallic derivatives of the ethereal salicylates with alkyl iodides at 100°–120°, *ethereal alkyl-ether* salicylates are obtained:



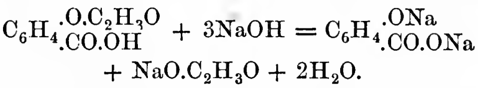
$$C_6H_4\genfrac{}{}{0pt}{}{.ONa}{.CO.O.CH_3} + ICH_3 = NaI + C_6H_4\genfrac{}{}{0pt}{}{.O.CH_3}{.CO.O.CH_3}$$

from which, on saponification and decomposition of the salts with acids, salicylic acid ethers are obtained, isomeric with the ethereal salicylates. *Methylic methyl-salicylate* is an oil boiling at 248°. *Methyl-salicylic acid,* $C_6H_4\genfrac{}{}{0pt}{}{.O.CH_3}{.CO.OH}$, crystallises in well-formed colourless tables, dissolving readily in alcohol, ether, and hot water, and melting at 98·5°; it is *not* coloured by ferric chloride. It unites with only *one* equivalent of metal and decomposes above 200° into carbonic anhydride and methyl-phenyl ether (anisol, § 960):



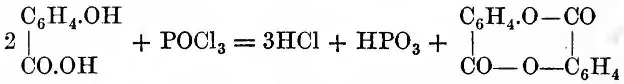
$$C_6H_4\genfrac{}{}{0pt}{}{.O.CH_3}{.CO.OH} = CO_2 + C_6H_5.O.CH_3.$$

By action of chlor-acetyl on salicylic acid *salicylic acid acetate,* $C_6H_4\genfrac{}{}{0pt}{}{.O.C_2H_3O}{.CO.OH}$, is formed, which crystallises in fine needles, and on treatment with alkalies yields dibasic salicylates and acetates:



$$C_6H_4\genfrac{}{}{0pt}{}{.O.C_2H_3O}{.CO.OH} + 3NaOH = C_6H_4\genfrac{}{}{0pt}{}{.ONa}{.CO.ONa}$$
$$+ NaO.C_2H_3O + 2H_2O.$$

This behaviour with the alcohol and acid radical haloids shows considerable analogy between salicylic acid and glycollic acid and its homologues, which is further exemplified by the formation of ethereal anhydrides. By the action of phosphoric oxychloride on salicylic acid or its salts *salicylide* is obtained, corresponding to glycollide and lactide:

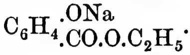
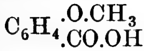
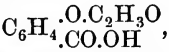


$$2\,\begin{array}{l}C_6H_4.OH\\ |\\ CO.OH\end{array} + POCl_3 = 3HCl + HPO_3 + \begin{array}{lcr}C_6H_4.O & - & CO\\ | & & |\\ CO & -\,O\,- & C_6H_4\end{array}$$

It is purified by extraction of the phosphoric acid by water and crystallisation of the residue from boiling absolute alcohol; it crystallises in concentrically grouped needles, melts above 200°, and is rapidly converted into salicylates by alkalies.

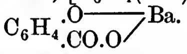
By the action of ammonia on ethereal salicylates *salicylamide,* $C_6H_4\genfrac{}{}{0pt}{}{.OH}{.CO.NH_2}$, isomeric with the amido-benzoic acids, is formed; it crystallises in yellow plates and melts at 142°.

By the action of the halogens (in the case of iodine in the presence of alkalies or of iodic acid) salicylic acid is readily converted into mono-, di-, and tri-halogen-substituted salicylic acids; fuming nitric acid converts it into nitro-salicylic acids (o. and p.) and dinitro-salicylic acid.

1063. *Metaoxy-benzoic acid*, frequently termed *oxybenzoic acid*, is obtained by passing nitrous anhydride into a dilute boiling aqueous solution of metamido-benzoic acid or by boiling metadiazo-benzoic acid nitrate with water. It is also readily obtained by fusing metahalogenated benzoic acids and metasulpho-benzoic acid with potassic hydrate, and similarly from metacresol. It forms a crystalline powder consisting of very small quadratic tables, sometimes aggregating to warty masses, is difficultly soluble in cold, more readily in hot water, melts at 200°, and can be to a great extent distilled unchanged, but on stronger heating decomposes into carbonic anhydride and phenol. It does not yield a violet colour with ferric chloride, but in other respects behaves analogously to salicylic acid. It gives normal and dibasic salts, ethereal salts, and the isomeric alkyl-ether metaoxy-benzoic acids, but does not yield ethereal anhydrides. *Ethylic meta-oxy-benzoate* is a solid, crystallising in tables, melting at 72°, and boiling at 282°. With cold concentrated sodic hydrate it yields crystals of the formula  $C_6H_4\begin{smallmatrix}.ONa\\.CO.O.C_2H_5\end{smallmatrix}$. Methyl-metaoxy-benzoic acid,  $C_6H_4\begin{smallmatrix}.O.CH_3\\.CO.OH\end{smallmatrix}$, crystallises in needles and melts at 95°. *Benzoic acid acetate*,  $C_6H_4\begin{smallmatrix}.O.C_2H_3O\\.CO.OH\end{smallmatrix}$, melts at 127°.

1064. *Paraoxy-benzoic acid* is usually obtained by heating potassic phenylate at 200° in a stream of carbonic anhydride, or from potassic salicylate at the same temperature. It is further obtained by passing nitrous anhydride into a hot aqueous solution of paramido-benzoic acid; by fusing parahalogen-benzoic acids, parasulpho-benzoic acid, paracresol, and many resins (e.g. aloe, dragon's blood, &c.), with alkalies.

Paraoxy-benzoic acid crystallises with one molecule of water in monoclinic prisms; when anhydrous it melts at 210°. It can be sublimed partly unchanged, but is at the same time in part decomposed into carbonic anhydride and phenol. It is more soluble in cold water than its isomerides.

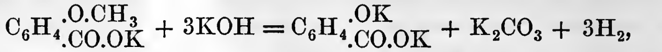
It does not produce any violet colour with ferric chloride, but gives an amorphous yellow precipitate, soluble in excess of ferric chloride. With regard to metallic and ethereal salts and ether-like compounds, it completely resembles its isomerides, giving, for example, a soluble neutral basic salt, $[C_6H_4(OH).CO.O]_2Ba$, and a difficultly soluble basic baric salt,  $C_6H_4\begin{smallmatrix}.O\\.CO.O\end{smallmatrix}\rangle Ba$.

Methylic paraoxy-benzoate, $C_6H_4(OH).CO.O.CH_3$, crystallises in tables and boils at 283°. *Ethylic paraoxy-benzoate* melts at 113° and boils at 297°.

1065. *Anisic acid*, or *methyl paraoxy-benzoic acid:*

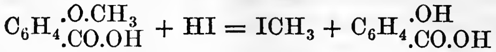
$$C_6H_4(O.CH_3).CO.OH,$$

is obtained from dibasic potassic paraoxy-benzoate by heating with methylic iodide, saponification of the salt, $C_6H_4(O.CH_3).CO.O.CH_3$, with potassic hydrate, and decomposition of the resulting potassic anisate with hydrochloric acid. It is still more readily obtained by oxidation of its aldehyde (§ 1033) or the anethol of anise oil with chromic acid. It crystallises from alcohol in large prisms, melts at 175°, sublimes unchanged, and is very difficultly soluble in cold water. When treated with the strongest bases it only unites with one equivalent of metal; it yields paraoxy-benzoic acid on fusion with potassic hydrate:



$$C_6H_4\genfrac{}{}{0pt}{}{.O.CH_3}{.CO.OK} + 3KOH = C_6H_4\genfrac{}{}{0pt}{}{.OK}{.CO.OK} + K_2CO_3 + 3H_2,$$

and gives methyl haloids and free paraoxy-benzoic acid on heating with fuming halogen hydro-acids:



$$C_6H_4\genfrac{}{}{0pt}{}{.O.CH_3}{.CO.OH} + HI = ICH_3 + C_6H_4\genfrac{}{}{0pt}{}{.OH}{.CO.OH}$$

By action of halogens paraoxy-benzoic acid and anisic acid are converted into halogen substitution products, by fuming nitric acid into mono- and dinitro-products.

Disubstituted Benzoic Acids.

1066. Three *dichlor-benzoic acids* are known. The 1:3:4 modification is obtained by the chlorination of either para- or metachlor-benzoic acid, and also by the oxidation of dichlor-toluene and of dichlor-benzyl chloride, $C_6H_3Cl_2.CH_2Cl$. It crystallises in colourless needles, melting at 202° and difficultly soluble in water. The 1:2:3 (or 1:2:5) derivative is obtained by the action of hydrochloric acid and potassic chlorate on benzoic acid, and by the action of antimonic chloride on orthochlor-benzoic acid; it crystallises in slender needles and melts at 156°. 1:2:4 dichlor-benzoic acid is obtained, together with the two preceding, by the action of water on dichlor-benzo-trichloride; it crystallises in small needles and melts at 126·5°. Three corresponding *dibrom-benzoic acids* have been prepared—1:3:5, melting at 208°–209°; 1:3:6 (or 1:2:5), melting at 151°–152°; and 1:3:4, melting at 229°–230°. *Dinitro-benzoic acids.* The longest known of these bodies, obtained by treatment of metanitro-benzoic acid with nitro-sulphuric acid, is the 1:2:4 compound; it melts at 204°. Orthonitro-benzoic acid, when similarly treated, yields three dinitro acids—1:2:5, melting at 140°; 1:2:4, melting at 179°; and 1:2:6, melting at 202°. Diamido-benzoic acids, chlor and brom nitro-benzoic acids, and disulpho-benzoic acids are also known, in each case in several isomers. Nitro- and halogen-substituted hydroxy-benzoic acids, anisic acids, &c., also belong to the same group, but their complete description would lead too far.

The *dihydroxy-benzoic acids*, or *diphenol benzoic acids:*

$$C_6H_3(OH)_2.CO.OH,$$

on the contrary, are of considerable importance. Of the six possible isomers four are known.

1067. 1. *Oxysalicylic* or *hydroxy-salicylic acid*, (1:2:5). On heating salicylic acid with iodine and iodic acid, mono- and diiodo-salicylic acid are formed, and can be separated by conversion into their sodic salts, that of moniodo-salicylic acid being more readily soluble. Pure iodo-salicylic acid is nearly insoluble in water and melts at

184°. When heated with the most concentrated potassic hydrate solution, till iodo-salicylic acid no longer separates on acidulating, it is converted into potassic oxy-salicylate, from which the free acid is liberated by sulphuric acid and separated by shaking with ether. Oxy-salicylic acid crystallises in shining needles, melts at 196°–197°, and requires 53 parts of water at 16° for solution. On dry distillation it yields hydroquinone together with some pyrocatechin. With ferric chloride it gives a deep blue colour.

2. *Protocatechuic acid*, (1:3:4), is a frequently occurring product of the decomposition of resins (guaiacum, dragon's blood, assafœtida, myrrh, &c.) by fusion with potassic hydrate, and is further obtained, by the same method, from the sulphonic acids of para- and meta-cresol, from iodo-paraoxybenzoic acid, catechin, quinic acid, vanilline, and other bodies. It crystallises with one molecule of water in plates and needles, dissolves in water, alcohol, and ether, and when dry melts at 199°. With ferric chloride it gives a dark bluish green coloration, which is changed to blue on addition of a small quantity of soda or to dark red with more of the latter. Dry distillation decomposes it into carbonic anhydride and pyrocatechin.

Ether-like derivatives of protocatechuic acid:—

Piperonylic acid, methene protocatechuic acid:

$$C_6H_3\left(\begin{matrix}O\cdot\\O\cdot\end{matrix}CH_2\right).CO.OH,$$

is obtained by oxidation of its aldehyde (§ 1034), and by heating protocatechuic acid with methene diiodide and potassic hydrate:

$$C_6H_3(OK)_2.CO.OK + CH_2I_2 = 2KI + C_6H_3\left(\begin{matrix}O\cdot\\O\cdot\end{matrix}CH_2\right).CO.OK.$$

It crystallises in colourless needles, which melt at 228° and can be sublimed.

Two modifications of methyl-protocatechuic acid:

$$C_6H_3(OH)(OCH_3).CO.OH,$$

are known:—

Vanillic acid, ($CO.OH:OCH_3:OH = 1:3:4$), is obtained by the oxidation of vanilline (§ 1034) and coniferine. It crystallises in white plates, melts at 211°–212°, and can be sublimed.

Isovanillic acid, ($CO.OH:OH:OCH_3 = 1:3:4$), obtained by heating protocatechuic acid with methylic iodide and potassic hydrate, melts at 250°.

Dimethyl-protocatechuic acid, $C_6H_3(OCH_3)_2CO.OH$, is identical with *veratric acid* (§ 1234).

Ethyl-methyl-protocatechuic acid, $C_6H_3(OCH_3)(OC_2H_5).CO.OH$, is obtained by the oxidation of ethyl eugenol; it melts at 190°.

3. Two *isomeric dioxy-benzoic acids* are obtained by fusion of the two disulpho-benzoic acids with potassic hydrate; the disulpho-acid obtained by the action of sulphuric anhydride on benzene yielding 1:2:3 *dioxy-benzoic acid*, melting at 220°, and giving no colour with ferric chloride; whilst the disulpho-benzoic acid, obtained by the oxidation of toluene disulphonic acid, gives 1:2:4 *dioxy-benzoic acid*, melting at 194° and giving a dark red coloration with ferric chloride.

Tri-substituted Benzoic Acids.

1068. *Gallic acid*, $C_7H_6O_5 = C_6H_2(OH)_3.CO.OH$ (1:2:4:5), a trioxybenzoic acid, is by far the most important of the tri-substituted benzoic acids. It occurs in the leaves of the wild vine, in mangoes, in divi-divi (fruit of *Caesalpina coriaria*), and also in small quantity in gall nuts, from which it can be obtained by boiling with water.

It can be obtained artificially from tannic acid by boiling with dilute acids or alkalies, by spontaneously occurring fermentation of solutions of tannic acid, and finally from *diiodo-salicylic acid*. This latter, obtained from the action of iodine and iodic acid on salicylic acid, and separated from moniod-salicylic acid as above described, yields protocatechuic acid when fused with alkalies, but potassic gallate when heated at 140°–150° with a solution of potassic carbonate.

Gallic acid crystallises from boiling water in fine silky needles, $C_7H_6O_5,H_2O$, which dissolve in 3 parts of boiling and 100 parts of cold water, readily in alcohol and ether. At 100° it loses the water of crystallisation, then melts at about 200°, and decomposes at 220° into carbonic anhydride and pyrogallol (§ 999). The aqueous solution gives a blackish blue precipitate with ferric chloride, and reduces solutions of the noble metals. Its normal salts, e.g.

$$C_6H_2(OH)_3.CO.OK,$$

are stable in the dry state, but in aqueous solution absorb oxygen and decompose. These oxidation processes occur especially quickly in solutions of the basic salts, which contain up to four equivalents of metal. Treated with chlor-acetyl, it yields colourless needles of *triaceto-gallic acid*, $C_6H_2(O.C_2H_3O)_3.CO.OH$. Bromine at ordinary temperatures converts it into brom- and dibrom-gallic acid, both crystalline compounds, of which the latter, $C_6Br_2(OH)_3CO.OH$, is a penta-substitution product of benzoic acid.

1069. *Tannic acid*, or *tannin*, $C_{14}H_{10}O_9$, stands in near relation to gallic acid, being probably its first ethereal anhydride:

$$C_6H_2(OH)_3.CO.O.C_6H_2(OH)_2.CO.OH.$$

It is formed from gallic acid by heating at 120° with phosphoric oxychloride, and by boiling its solutions with arsenic acid. It forms a chief constituent of the ordinary and Chinese gall nuts and of sumach (leaves of *Rus coriaria*), from which it may be extracted by twice repeated long maceration of the powdered substances with double the quantity of a mixture of four parts ether and one part alcohol. The filtered solution is then mixed with a quantity of water equal to $1\frac{1}{2}$ time the weight of the gall nuts, the alcohol and ether evaporated, and the aqueous solution finally brought to dryness on the water bath.

Tannin is an amorphous shining mass, readily soluble in water, of strong astringent taste and weak acid reaction. Its aqueous solution is precipitated by mineral acids and many alkaline salts, and gives a bluish black precipitate with ferric salts (ink). It also gives a precipitate with gelatine solutions, and is removed from its solutions by gelatinous tissue, the different varieties of leather being formed. It further gives precipitates with tartar emetic, starch solution, albumin, and nearly all alkaloids. Boiled with excess of acetic anhydride, it gives *pentaceto-tannin*, $C_{14}H_5(C_2H_3O_2)_5O_9$, melting at 137°.

It forms neutral and basic salts, the latter absorbing oxygen from the air and becoming brown-coloured.

On exposing an aqueous solution of tannin for a long time to the action of the air, a deposit is obtained which is a mixture of gallic acid together with ellagic acid, an oxidation product of tannin.

1070. *Ellagic acid*, $C_{14}H_8O_9,H_2O$, is also obtained by heating gallic acid with dry arsenic acid at 130°–160°, by long heating of solutions of tannin or gallic acid with iodine, and forms the main constituent of bezoar stones (an intestinal calculus of the Persian goat). Ellagic acid forms a pale yellow microcrystalline powder, nearly insoluble in water, difficultly soluble in alcohol, and forming readily soluble salts with acids. At 100° it loses its water of crystallisation, and at 200° a second molecule of water, being converted into an anhydride derivative, $C_{14}H_6O_8$.

1071. *Quinic acid*, $C_7H_{12}O_6$, occurs chiefly in the cinchona barks as a quinine salt, but is also found in many other plants, such as the bilberry, coffee beans, &c.

On precipitating the quinine alkaloids from the sulphuric acid extract of the bark, with milk of lime, it remains in solution as calcic salt, which, on evaporation of the solution, is obtained in large efflorescent rhombic crystals of the formula $(C_7H_{11}O_6)_2Ca,10H_2O$. By decomposition of the aqueous solution of this salt with oxalic acid and evaporation of the filtrate, quinic acid crystallises in oblique rhombic prisms. It is readily soluble in water and melts at 162°. Its aqueous solution rotates the plane of polarisation of light to the left. The normal salts are mostly soluble and contain one equivalent of metal, but basic salts are also known, e.g. of lead and copper.

On dry distillation quinic acid yields hydroquinone, pyrocatechin, benzoic acid, phenol, &c.; by treatment with oxidising agents, e.g. by heating with manganic dioxide and dilute sulphuric acid, it is converted into formic acid, carbonic anhydride, and quinone. Gently heated with phosphoric chloride, it yields metachlor-benzoyl chloride, $C_6H_4Cl.CO.Cl$; by heating with concentrated hydriodic acid, only benzoic acid. Fusion with caustic potash or the action of bromine on its aqueous solution converts it into protocatechuic acid.

It can therefore be regarded as the hexhydride of a tetroxybenzoic acid (comp. § 947, 2), $C_6H_7(OH)_4.CO.OH$.

HOMOLOGUES OF BENZOIC ACID.

Acids of the Formula $C_8H_8O_2$.

1072. *Phenyl-acetic acid*, or *α-toluic acid*, $C_6H_5.CH_2.CO.OH$, is generally prepared from benzylic chloride (§ 1027) by heating with potassic cyanide and alcohol, when *benzyl cyanide*, or phenyl acetonitril, $C_6H_5.CH_2.CN$, boiling at 229°, is obtained, and this decomposed by boiling with alkalies. It is also synthesised as its ethylic salt by heating a mixture of brom-benzene and ethylic chlor-acetate with powdered copper at 200°:

$$C_6H_5Br + Cl.CH_2.CO.O.C_2H_5 + Cu_2 = Cu_2BrCl$$
$$+ C_6H_5.CH_2.CO.O.C_2H_5.$$

It is obtained from mandelic acid by reduction with hydriodic acid, from vulpinic acid by decomposition with baryta, and from atropic acid by fusion with potassic hydrate. Phenyl-acetic acid crystallises in shining plates, melts at 76·5°, and boils at 262°. Bromine and nitric acid in the cold convert it into para-substitution products.

Benzylic cyanide, mentioned above, occurs in the ethereal oil of *Tropaeoleum majus.*

1073. *Toluic acids,* or *methyl benzoic acids,*  $C_6H_4\begin{matrix}.CH_3\\.CO.OH\end{matrix}$, are known in three modifications, ortho, meta, and para. The first and last are formed by the oxidation of the respective xylenes (§ 1021) with dilute nitric acid :

$$C_6H_4(CH_3)_2 + 3O = C_6H_4(CH_3).CO.OH + H_2O,$$

and can be separated from the nitro products formed at the same time by distillation with water vapour.

Metaxylene, when pure, is not attacked by nitric acid, but is when mixed with paraxylene, yielding a mixture of meta- and para-toluic acids, which cannot be completely separated.

1. *Ortho-toluic acid* is usually prepared from its nitril, *ortho-cyano-toluene,* by decomposition with alcoholic potassic hydrate or hydrochloric acid. It crystallises in long fine needles, melts at 102°, and is difficultly soluble in cold, readily in hot water. Oxidation with chromic and sulphuric acid converts it not into phthalic acid, but into carbonic anhydride and water (comp. § 954). On the other hand, much phthalic acid is obtained by employment of exactly the necessary amount of potassic permanganate in alkaline solution. The *calcic salt,* $[C_6H_4(CH_3).CO.O]_2Ca,2H_2O$, crystallises in needles and is readily soluble in water. Concentrated nitric acid converts it into *nitro-ortho-toluic acid,* $C_6H_3(NO_2)(CH_3).CO.OH$, melting at 145°. *Ortho-cyano-toluene,* $C_6H_4(CH_3).CN$, is prepared from ortho-toluidine (§ 1014) by first converting it into isosulphocyanate and then heating this with powdered copper. It is an oil of bitter almond-like odour, boiling at 203°–204°.

2. *Metatoluic acid* is obtained in a state of purity by heating uvitic acid with lime :

$$2C_6H_3(CH_3)(CO.OH)_2 + 3Ca(OH)_2 = 2CaCO_3 + 4H_2O \\ + [C_6H_4(CH_3)CO.O]_2Ca.$$

It crystallises in needles, melts at 109°–110°, and is more readily soluble in water than the preceding. Chromic and sulphuric acid oxidise it to isophthalic acid. The readily soluble calcic salt :

$$(C_8H_7O_2)_2Ca,3H_2O,$$

crystallises in spear-shaped needles.

3. *Paratoluic acid* is obtained by treating parabrom-toluene (§ 1012) with sodium and carbonic anhydride :

$$CH_3.C_6H_4.Br + CO_2 + Na_2 = NaBr + CH_3.C_6H_4.CO.ONa,$$

or by saponification of *paracyano-toluene* (a crystalline mass melting at 38°, obtained from paratoluidine by conversion into isosulphocyanate, &c., or from potassic paratoluene sulphonate by dry distillation with potassic cyanide). It crystallises in needles, melts at 178°, and is very difficultly soluble in cold water. On oxidation it yields terephthalic acid; its calcic salt, $(C_8H_7O_2)_2Ca,3H_2O$, crystallises in shining prisms, which are readily soluble. With concentrated nitric acid it yields *nitro-paratoluic acid*, melting at 189°–190°.

All three toluic acids yield toluene when distilled with lime:

$$C_6H_4\begin{smallmatrix}.CH_3\\ .CO.OH\end{smallmatrix} + Ca(OH)_2 = CaCO_3 + H_2O + C_6H_5.CH_3.$$

Acids of the Formula $C_9H_{10}O_2$.

1074. *Phenyl-propionic acids*, $C_6H_5.C_2H_4.CO.OH$. Two are known, hydrocinnamic acid and hydratropic acid.

Hydrocinnamic acid, or *β-phenyl-propionic acid*, is obtained by the action of nascent hydrogen on cinnamic acid, $C_9H_8O_2$, by careful oxidation of primary phenyl-propyl alcohol (§ 1030), and from its nitrile, *phenethyl cyanide*, $C_6H_5.CH_2.CH_2.CN$, by heating with hydrochloric acid. This latter occurs in oil of watercress (*Nasturtium officinale*), and can be obtained by the action of potassic cyanide on styryl chloride (§ 1029). It is an oil boiling at 261° and of sp. gr. 1·0014 at 18°.

Hydrocinnamic acid is readily soluble in ether, alcohol, and boiling water, difficultly in cold water; it melts at 47° and boils at 280°. Chromic acid oxidises it to benzoic acid; fuming nitric acid converts it into *paranitro-hydrocinnamic acid*, forming flat needles, melting at 164°.

Hydratropic acid, $C_6H_5.CH\begin{smallmatrix}.CH_3\\ .CO.OH\end{smallmatrix}$, or *a-phenyl-propionic acid*, is formed by addition of hydrogen to atropic acid; it is a liquid which does not crystallise.

1075. *Ethyl-benzoic acids*, $C_6H_4\begin{smallmatrix}.C_2H_5\\ .CO.OH\end{smallmatrix}$. Of these only the para compound has been prepared, by the action of sodium and carbonic anhydride on parabrom-ethyl-benzene:

$$C_2H_5.C_6H_4.Br + Na_2 + CO_2 = NaBr + C_2H_5.C_6H_4.CO.ONa,$$

and by oxidation of paradiethyl-benzene (§ 1023) with dilute nitric acid. It forms plates resembling benzoic acid, and melts at 110°. Chromic acid oxidises it to terephthalic acid.

1076. *Dimethyl-benzoic acids*, $C_6H_3\begin{cases}(CH_3)_2\\ CO.OH\end{cases}$. Of these three isomers are known.

Mesitylenic acid, (1:3:5), is formed by the oxidation of mesitylene with dilute nitric acid. It crystallises from boiling water in needles, from alcohol in large prisms, melts at 166°, and can be sublimed. Dry distillation with lime converts it into metaxylene (§ 1021); by oxidation with chromic acid it is converted into the dibasic uvitic acid (§ 1111), and finally into the tribasic trimesic acid (§ 1113, 1). Its baric salt, $(C_9H_9O_2)_2Ba$, crystallises in large prisms, readily soluble in water.

Xylic acid, $(CO.OH:CH_3:CH_3 = 1:2:4)$, is prepared from brom-metaxylene by means of sodium and carbonic anhydride. Like the preceding, it is difficultly soluble in water, more readily in alcohol, from which it crystallises in large monoclinic prisms, melting at 126°. It yields metaxylene when distilled with lime. Its *calcic salt:*

$$(C_9H_9O_2)_2Ca,2H_2O,$$

crystallises in large prisms.

By oxidation of pseudocumene with dilute nitric acid xylic acid is obtained together with

Paraxylic acid, (1:3:4), which can be separated from the former by means of its *calcic salt,* $2(C_9H_9O_2)_2Ca,7H_2O$, which crystallises in bunches of brittle needles. The free acid crystallises from alcohol in concentrically grouped spear-like needles. It yields orthoxylene when distilled with lime.

Paramethyl-phenyl-acetic acid, $C_6H_4\begin{matrix}.CH_3\\.CH_2.CO.OH\end{matrix}$, or *a-xylic acid,* is prepared from its nitrile, tolyl cyanide (comp. § 1029, 1), in the usual manner, in the form of broad shining plates, melting at 42°. It dissolves readily in hot water.

Acids of the Formula $C_{10}H_{12}O_2$.

1077. 1. *Cumic acid,* $C_6H_4\begin{matrix}.C_3H_7\\.CO.OH\end{matrix}$, a parapropyl benzoic acid, is formed, together with cuminic alcohol, when their aldehyde (§ 1035) is heated with alcoholic potassic hydrate. It crystallises in tables or prisms, only readily soluble in alcohol or ether, melts at 114°–115°, and can be sublimed. Chromic acid oxidises it to terephthalic acid.

2. *Durylic acid,* a trimethyl benzoic acid, $C_6H_2\left\{\begin{matrix}(CH_3)_3\\CO.OH\end{matrix}\right.$, is obtained by oxidation of durene (§ 1025) with boiling aqueous nitric acid. It crystallises from alcohol in hard shining prisms, melts at 149°–150°, and is scarcely dissolved by boiling water.

1078. *Homocuminic acid,* $C_{11}H_{14}O_2$, or *parapropyl-phenyl acetic acid,* $C_6H_4\begin{matrix}.C_3H_7\\.CH_2.CO.OH\end{matrix}$, is obtained from its nitrile, and this from cumin alcohol by conversion into chloride and decomposition with potassic cyanide. It melts at 52°.

AROMATIC HYDROXY-ACIDS.

1079. The aromatic hydroxy-acids, to which group the hydroxy derivatives of benzoic acid previously mentioned also belong, appear by their formula as homologues of the latter, but this is truly the case only when the hydroxyl substitution occurs at the benzene group, in which case the hydroxy-acids have the properties of phenols also. Such compounds may arise both from the alkyl benzoic acids and from the aromatised fatty acids (comp. § 1044); e.g.

$$\underset{\text{Cresotic acids.}}{C_6H_3\left\{\begin{matrix}OH\\CH_3\\CO.OH\end{matrix}\right.} \quad\text{and}\quad \underset{\text{Melitolic acid.}}{C_6H_4\left\{\begin{matrix}OH\\CH_2.CH_2.CO.OH\end{matrix}\right.}$$

If the substitution occurs in the aromatised fatty acids at the groups C_nH_{2n} lying between the benzene nucleus and the CO.OH group, aromatic derivatives of the alcohol acids are obtained; e.g. phenyl glycollic acid, $C_6H_5.CH(OH).CO.OH$. Finally, in the alkyl benzoic acids the substitution can occur in the alkyl group, so that aromatic alcohol acids result, like § 1082.

In the case of the hydroxylated acids many combinations of these varieties of substitution might occur, so that the number of possible isomers is very large.

Monohydroxy-Acids of the Formula $C_nH_{2n-8}(OH).CO.OH$.

Acids of the Formula $C_7H_6(OH)CO.OH$.

1080. *Hydroxy-toluic acids,* $C_6H_3(OH)\begin{smallmatrix}.CH_3\\ .CO.OH\end{smallmatrix}$. Of the numerous possible isomers five are known. Three, the *cresotic acids,* are prepared by the action of sodium and carbonic anhydride on the three modifications of cresol:

$$C_6H_4(OH).CH_3 + Na_2 + CO_2 = C_6H_3(ONa)(CH_3).CO.ONa + H_2.$$

They crystallise in needles, and in aqueous solution give violet colorations with ferric chloride. Without doubt they contain the hydroxyl and CO.OH groups in neighbouring (ortho) positions, and are therefore methylised salicylic acids. *α-Cresotic acid,* from paracresol, melts at 147°–150°; *β-cresotic acid,* from ortho-cresol, at 164°; and *γ-cresotic acid,* from metacresol, at 174°.

α-Oxytoluic acid, obtained by fusion with caustic potash of the sulpho-paratoluic acid, obtained by oxidation of thio-cymophenol (§ 1023), crystallises in needles and melts at 202°–203°.

β-Oxytoluic acid is obtained from nitro-paratoluic acid by reduction to amido-paratoluic acid and decomposition of the latter with nitrous acid in boiling aqueous solution. It crystallises in needles grouped in star-like forms, and melts at 183°–184°. Both oxytoluic acids give no coloration with ferric chloride.

1081. *Phenyl glycollic acid,* $C_6H_5.CH(OH).CO.OH$, or *mandelic acid,* is obtained from benzaldehyde in the same manner as lactic acid from acetic aldehyde. Benzaldehyde unites directly with hydrocyanic acid, forming benzylidene hydrate cyanide, $C_6H_5.CH(OH).CN$, whose aqueous solution, on boiling with hydrochloric acid, is converted into ammonic chloride and mandelic acid. The solution is evaporated to dryness on the water bath and the mandelic acid extracted with ether. It crystallises in prisms or tables, is readily soluble in water, and melts at 115°; oxidising agents convert it into carbonic anhydride and benzoic aldehyde or acid. Hydrochloric or hydrobromic acids readily convert it into phenyl-chlor- or phenyl-brom-acetic acids:

$$C_6H_5.CH(OH).CO.OH + HBr = H_2O + C_6H_5.CHBr.CO.OH.$$

Hydriodic acid, on heating, reduces it to phenyl acetic acid:

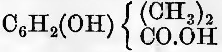
$$C_6H_5.CH(OH).CO.OH + 2HI = I_2 + H_2O + C_6H_5.CH_2.CO.OH.$$

These reactions place mandelic acid in very close relationship to the acids of the lactic series.

1082. *Oxymethyl-phenyl formic acid,* $C_6H_4\begin{smallmatrix}.CH_2.OH\\ .CO.OH\end{smallmatrix}$, is obtained from paratoluic acid by heating with bromine and boiling the resulting compound, $C_6H_4(CH_2Br).CO.OH$, with baryta water. Addition of hydrochloric acid liberates the free acid from the baric salt. It crystallises in flat needles, melting at 176°.

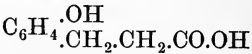
Acids of the Formula $C_8H_8(OH).CO.OH$.

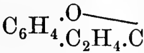
1083. *Phenol Acids.*—To these belong—

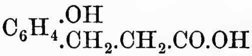
1. *Oxymesitylenic acid,*  $C_6H_2(OH)\begin{cases}(CH_3)_2\\ CO.OH\end{cases}$ (1:3:4), obtained by heating mesitylene sulphonic acid with potassic hydrate at 250°:

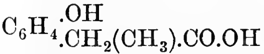
$$C_6H_2(SO_2.OK)(CH_3)_3 + 3KOH = K_2SO_3$$
$$+ C_6H_2(OK)(CH_3)_2.CO.OK + 3H_2.$$

It crystallises in fine silky needles, melting at 176°, and is nearly insoluble in cold water. Its salts give a deep blue coloration with ferric chloride, and yield solid xylenol on heating with potassic hydrate.

2. *Melilotic acid,* or *hydrocoumaric acid,*  $C_6H_4\genfrac{}{}{0pt}{}{.OH}{.CH_2.CH_2.CO.OH}$ (1:2), occurs in the yellow melilot (*Melilotus officinalis*), and is prepared from coumaric acid by addition of hydrogen.

It crystallises in prisms melting at 82°, which are pretty readily soluble in hot water. At higher temperatures it yields the ethereal anhydride  $C_6H_4\genfrac{}{}{0pt}{}{.O\text{———}}{.C_2H_4.CO}$, crystallising in tables, melting at 25° and boiling at 272°. Fusion with potassic hydrate converts melilotic acid into potassic salicylate and acetate. Melilotic acid is therefore an ortho-benzene derivative.

3. *Hydro-paracoumaric acid,*  $C_6H_4\genfrac{}{}{0pt}{}{.OH}{.CH_2.CH_2.CO.OH}$ (1:4), is formed by addition of hydrogen to paracoumaric acid, also from nitrophenyl propionic acid by reduction to the amido-acid and decomposition of this by nitrous acid. It melts at 125° and is readily soluble in water.

4. *Phloretic acid,*  $C_6H_4\genfrac{}{}{0pt}{}{.OH}{.CH_2(CH_3).CO.OH}$ (1:4), is prepared from its glucoside, *phloridzine,* $C_{21}H_{24}O_{10},2H_2O$. This latter occurs in the root bark of fruit trees, especially of apple and pear trees, from which it can be extracted by boiling with dilute alcohol. Tannin and other impurities are removed from the solution by precipitation with basic plumbic acetate, the filtrate treated with hydric sulphide to remove lead, and then evaporated.

Phloridzine forms fine silky needles of bitter taste, melting, when anhydrous, at 106°–109°. At 130° the mass again solidifies, probably with conversion into an isomeric modification, and becomes liquid once more at 160°; in aqueous solution this modification is slowly retransformed into ordinary phloridzine. In presence of ammonia phloridzine absorbs oxygen, acquiring a purple colour and being converted into phloridzeïn:

$$C_{21}H_{24}O_{10} + 2NH_3 + 3O = C_{21}H_{30}N_2O_{13}.$$

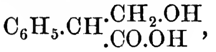
On boiling with dilute acids, phloridzine splits up into glucose and *phloretine*, $C_{15}H_{14}O_5$, which on cooling separates in colourless plates. Phloretine is a salt of phloretic acid and phloroglucin (§ 1000), and is decomposed into these on evaporation with solution of potassic hydrate.

When the dry alkaline mass is extracted with alcohol, potassic phloretate dissolves, whilst potassium phloroglucin remains behind. Phloretic acid crystallises in long colourless prisms, melting at 128°–130°; it is readily soluble in alcohol, ether, or hot water, and gives a green colour with ferric chloride. It forms normal and basic salts, and is converted into paraoxy-benzoic and acetic acids on fusion with potassic hydrate, and into phlorol (§ 1018) and carbonic anhydride on distillation with lime.

1084. *Phenyl lactic acids*, $C_6H_5.C_2H_3(OH).CO.OH$. Two isomeric acids of this formula are known.

1. *Phenyl lactic acid*, probably β-phenyl-α-hydroxy-propionic acid, $C_6H_5.CH_2.CH(OH).CO.OH$, is obtained by the action of sodium amalgam on phenyl-chlor-lactic acid ($C_6H_5.CHCl.CH(OH).CO.OH$, obtained by action of hypochlorous acid on cinnamic acid) or phenyl brom-lactic acid. It crystallises in pointed needles readily soluble in cold, still more so in hot water, melts at 93°–94°, and decomposes at 180° into water and cinnamic acid. Concentrated halogen hydro-acids convert it into phenyl halogen propionic acids.

2. *Tropic acid*, which, from its decompositions and its connection with atropic acid, is probably α-phenyl-β-hydroxy-propionic acid:

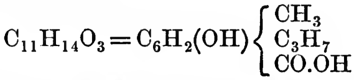


$$C_6H_5.CH\begin{matrix}.CH_2.OH\\.CO.OH\end{matrix},$$

is formed by heating atropic acid and concentrated hydrochloric acid at 180° for several hours. It dissolves in 49 parts of water at 14·5°, is more readily dissolved in alcohol and ether; it crystallises in prisms and melts at 117°. By long heating with hydrochloric acid it loses water and is converted into atropic and isatropic acids.

Higher Homologues.

1085. The isomeric phenols thymol and carvacrol (§ 1023) are converted by the action of carbonic anhydride and sodium into two isomeric acids of the formula:



$$C_{11}H_{14}O_3 = C_6H_2(OH)\begin{cases}CH_3\\C_3H_7\\CO.OH\end{cases}$$

thymotic and *carvacrotic acids*, both giving intensely blue colorations with ferric chloride. *Thymotic acid* crystallises in fine needles; it melts at 120°, cannot be sublimed unchanged, and is difficultly soluble in water. Heated with phosphoric anhydride, it yields an ethereal anhydride, *thymotide*, $C_{11}H_{12}O_2$, which is crystalline and melts at 187°. *Carvacrotic acid* forms flat needles, melting at 133°–134°.

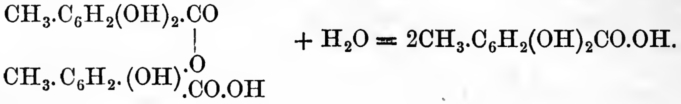
Dihydroxy-Acids of the Formula $C_nH_{2n-9}(OH)_2.CO.OH$.

1086. *Orsellinic acid*, $C_6H_2(CH_3)(OH)_2.CO.OH$, is obtained from lecanoric acid or erythrine by boiling for a short time with baryta or lime water. It crystallises in colourless prisms of both acid and bitter taste; it is readily soluble in water, alcohol, and ether, and decomposes at 176° into carbonic anhydride and orcin (§ 1016):

$$CH_3.C_6H_2(OH)_2.CO.OH = CO_2 + CH_3.C_6H_3(OH)_2.$$

It gives a purple violet coloration with ferric chloride. With the alkalies and alkaline earths it gives monobasic normal salts, which on boiling, especially in presence of excess of base, decompose into orcin and carbonate.

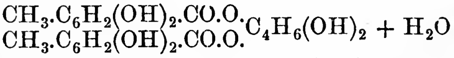
Lecanoric acid, $C_{16}H_{14}O_7,H_2O$, is an ethereal anhydride of orsellinic acid; it occurs in several lichens of the genera *Rocella* (especially *R. tinctoria*), *Lecanora*, and *Variolaria*, from which it can be extracted with ether. It crystallises in colourless needles, nearly insoluble in water. On boiling with water it splits into two molecules of orsellinic acid:



$$\begin{array}{l}CH_3.C_6H_2(OH)_2.CO\\ \qquad\qquad\qquad\quad |\\ CH_3.C_6H_2.(OH)\begin{array}{l}.O\\ .CO.OH\end{array}\end{array} + H_2O = 2CH_3.C_6H_2(OH)_2CO.OH.$$

On boiling with alcohol it yields the corresponding ethylic orsellinate, $CH_3.C_6H_2(OH)_2.CO.O.C_2H_5$, also crystallising in needles.

Erythrin, or erythrite diorsellinate, $C_{20}H_{22}O_{10}$, occurs in *Rocella fuciformis*, from which it can be extracted by means of cold milk of lime. The liquid is filtered quickly and saturated with carbonic anhydride, and the precipitate, consisting of calcic carbonate and erythrin, treated with alcohol to extract the latter. Erythrin crystallises in needles combined to spherical aggregates; it is nearly insoluble in cold water, and on long boiling with the latter is converted into orsellinic acid and *picro-erythrin*, or erythrite mono-orsellinate:

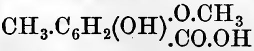


$$\begin{array}{l}CH_3.C_6H_2(OH)_2.CO.O.\\ CH_3.C_6H_2(OH)_2.CO.O.\end{array}C_4H_6(OH)_2 + H_2O$$

$$= CH_3.C_6H_2(OH)_2CO.OH + CH_3.C_6H_2(OH)_2.CO.O.C_4H_6(OH)_3.$$

Picro-erythrin forms crystals of bitter taste, $C_{12}H_{16}O_7,H_2O$, and on boiling with lime water is converted into carbonic acid, orcin, and erythrite (§ 770).

1087. *Everninic acid*, $C_9H_{10}O_4$, and *evernic acid*, $C_{17}H_{16}O_7$, also belong to the derivatives of orsellinic acid. Evernic acid is obtained from the lichen *Evernia prunastri* by treatment with milk of lime and precipitation with hydrochloric acid. It is insoluble in water, and by boiling with lime water for not too long a time is decomposed into everninic acid and orsellinic acid, or carbonic acid and orcin. *Everninic acid* crystallises in fine needles, melting at 157°, readily soluble in alcohol, ether, and boiling water, nearly insoluble in cold water. It is coloured violet by ferric chloride. By fusion with potassic hydrate it yields orcin and carbonic acid. From this everninic acid appears to be methyl orsellinic acid:



$$CH_3.C_6H_2(OH)\begin{array}{l}.O.CH_3\\ .CO.OH\end{array}$$

and evernic acid an ethereal anhydride of everninic and orsellinic acids.

1088. Two acids are known isomeric with everninic acid—hydrocaffeic acid and umbellic acid. They are probably both represented by the formula $C_6H_3(OH)_2.C_2H_4.CO.OH$.

Hydrocaffeic acid is obtained by the action of sodium amalgam on caffeic acid, $C_9H_8O_4$. It forms colourless rhombic prisms, readily soluble in cold water. It yields amorphous salts, which decompose on exposure to air from oxidation, whose solutions reduce ammoniacal solutions of copper and silver and give a dark cherry-red colour with ferric chloride.

From its connection with caffeic acid it would appear to have the formula $(HO)_2:C_6H_3.CH_2.CH_2.CO.OH$. On fusion with potassic hydrate it yields pyrocatechin.

Umbellic acid, which yields resorcin on fusion with potassic hydrate, is obtained by the action of sodium amalgam on an alkaline solution of umbelliferone, $C_9H_6O_3$. It forms colourless granular crystals, melting below 125° and difficultly soluble in cold water. Its salts also oxidise on exposure to air, and reduce alkaline silver and copper solutions.

1089. *Tyrosine*, $C_9H_{11}NO_3$, doubtless belongs to the disubstitution products of monobasic aromatic acids of the formula $C_9H_{10}O_2$. It has not yet been prepared synthetically, but has only been obtained, together with leucine (§ 750), aspartic acid (§ 863), and glutamic acid (§ 866, 3), as a decomposition product of different albuminoids, equally whether the decomposition has been effected by fusing alkalies, by acids, or as in putrefaction by the action of ferment-like bodies. This last method of formation explains its occurrence in the animal organism. It is best obtained in large quantity by boiling horn shavings with a mixture of 2 parts sulphuric acid and 8 parts water for twelve hours, the water evaporated being replaced; the liquid is then rendered alkaline by milk of lime, the filtrate evaporated to a small volume and over-saturated with acetic acid. On long standing tyrosine separates, whilst leucine, &c., remain in solution. It is purified by hot water, and then forms bunches of fine silky needles, soluble in 150 parts of boiling water and 1,900 parts of cold water, scarcely soluble in alcohol, insoluble in ether. It can be recognised by the red colour obtained when its solution is heated with mercuric nitrate and nitrous acid, and by the violet coloration on heating with sulphuric acid, neutralising with baric carbonate, and adding ferric chloride.

Tyrosine dissolves readily in mineral acids, forming saline compounds, e.g. $C_9H_{11}NO_3.HCl$, crystallising in needles; it also dissolves in ammonia solution and caustic alkalies. With baryta water it gives prisms of *barium tyrosine*, $C_9H_9BaNO_3,2H_2O$. By mixing tyrosine solutions with argentic nitrate two compounds ($C_9H_{10}AgNO_3$, which is crystalline, and $C_9H_9Ag_2NO_3$, a precipitate) are obtained according to the concentration and quantity of the silver solution. Tyrosine behaves similarly to the glycines. By fusion with potassic hydrate it yields ammonia and the potassic salts of paraoxybenzoic and acetic acids; by the action of chlorine and bromine it gives *chloranil* and bromanil (§ 1005). From this tyrosine is probably a para compound of the formula $NH_2.C_6H_4.C_2H_3(OH).CO.OH$, or

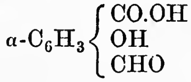
$$HO.C_6H_4.C_2H_3(NH_2).CO.OH.$$

Excess of dilute nitric acid converts tyrosine into brownish yellow crystals of nitro-tyrosine nitrate, $C_9H_{10}(NO_2)NO_3,HNO_3$, from whose aqueous solution ammonia precipitates sulphur-yellow needles of *nitro-tyrosine*, $C_9H_{10}(NO_2)NO_3$. On heating with nitric acid *dinitro-tyrosine*, $C_9H_9(NO_2)_2NO_3$, is formed, crystallising in golden yellow plates; it does not yield salts with acids. Concentrated sulphuric acid converts tyrosine into several *sulphonic acids*, e.g.

$$C_9H_{10}(SO_2.OH)NO_3,$$

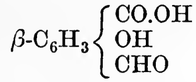
whose baric salts are coloured violet by ferric chloride.

1089*a*. *Aldehyde Acids.*—But few of these bodies are known at present. They are prepared by boiling the oxybenzoic acids with sodic hydrate, water, and chloroform. Salicylic acid thus treated gives rise to two *aldehydo-salicylic acids :*



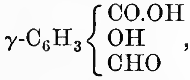
$$\alpha\text{-}C_6H_3\begin{cases}CO.OH\\OH\\CHO\end{cases}$$

(1:2:3) forms slender needles, which can be sublimed; its solution is coloured red by ferric chloride.



$$\beta\text{-}C_6H_3\begin{cases}CO.OH\\OH\\CHO\end{cases}$$

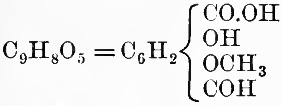
(1:2:5) forms slender needles, melts at 249°, and can be sublimed, and gives a cherry-red colour with ferric chloride.



$$\gamma\text{-}C_6H_3\begin{cases}CO.OH\\OH\\CHO\end{cases}$$

, prepared from paraoxy-benzoic acid, crystallises in prisms, melts at 243°–244°, is sublimable, and gives a brick-red colour with ferric chloride.

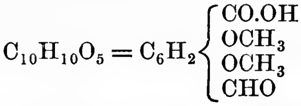
Aldehydo-vanillic acid, or *aldehydo-methyl-protocatechuic acid*,



$$C_9H_8O_5 = C_6H_2\begin{cases}CO.OH\\OH\\OCH_3\\COH\end{cases}$$

, crystallises in silky needles, melts at 221°–222°, and gives a violet colour with ferric chloride.

Opianic acid, aldehydo-dimethyl protocatechuic acid :



$$C_{10}H_{10}O_5 = C_6H_2\begin{cases}CO.OH\\OCH_3\\OCH_3\\CHO\end{cases}$$

is described under the opium derivatives (§ 1265).

CINNAMIC GROUP.

1090. The chief representatives of the cinnamic group can be viewed as phenyl derivatives of allyl alcohol, acroleïn, and acrylic acid, just as the aromatic alcohols, aldehydes, and acids previously described may be considered as the phenyl substitution products of the alcohols $C_nH_{2n+1}.OH$, their aldehydes, and the fatty acids. The compounds in this group all contain phenyl in combination with a tricarbon nucleus, in which two of the carbon atoms are in divalent union.

Cinnamic Alcohol.

1091. *Styryl alcohol*, or *phenyl-allyl alcohol:*

$$C_9H_{10}O = C_6H_5.CH:CH.CH_2.OH,$$

is obtained by distillation of its cinnamate with potassic hydrate, also in smaller quantity by heating cinnamic aldehyde with alcoholic potassic hydrate (comp. § 1026). It crystallises in needles of hyacinth-like odour, melts at 33°, distils at 250°, is difficultly soluble in water, readily in alcohol and ether. It is converted into cinnamic acid on careful oxidation, and when treated with the halogen hydro-acids yields styryl haloids—e.g. *styryl chloride*, C_9H_9Cl, and *styryl iodide*—which unite with ammonia to *styryl ammonic chloride*, $C_9H_9NH_3Cl$, &c. On gentle heating of styryl alcohol and boron trioxide *styryl ether*, $(C_9H_9)_2O$, is obtained as an oily liquid.

Styryl alcohol unites directly with bromine, when the two ingredients in solution in chloroform are mixed, forming *cinnamic alcohol dibromide*, or *styryl dibromide hydrate*, $C_6H_5.CHBr.CHBr.CH_2.OH$ (comp. § 681), which crystallises from alcohol or ether in colourless needles or tables melting at 74°. By heating with concentrated hydrobromic acid it is converted into styryl tribromide:

$$C_6H_5.CHBr.CHBr.CH_2Br,$$

forming shining needles, melting at 124°. This, on long heating with water, is converted into the trivalent alcohol:

$$C_6H_5.CH(OH).CH(OH).CH_2(OH),$$

stycerine, or *phenyl glycerin*, readily soluble in water and alcohol and left on evaporation as a gummy mass.

1092. *Cinnamic aldehyde*, $C_9H_8O = C_6H_5.CH:CH.CHO$, forms the chief constituent of the essential oil of cinnamon and cassia; it is obtained by oxidation of cinnamic alcohol by aid of platinum black, and is prepared synthetically by saturation of a mixture of benzaldehyde and acetic aldehyde with hydrochloric acid (comp. § 765):

$$C_6H_5.CHO + CH_3.CHO = H_2O + C_6H_5.CH{:}CH.CHO.$$

It forms a difficultly soluble crystalline compound with hydric sodic sulphite, and can thus be readily separated from cinnamic alcohol and obtained on heating the purified crystals with soda solution.

Cinnamic aldehyde is a colourless oil of strong cinnamon odour, heavier than water; on exposure to air it absorbs oxygen and is slowly converted into cinnamic acid. It boils at 247°–248° with slight decomposition and volatilises readily in water vapour. It reacts with dry ammonia, yielding water and *hydrocinnamide* (comp. § 1031):

$$3C_6H_5.C_2H_2.CHO + 2NH_3 = 3H_2O + (C_6H_5.C_2H_2.CH{:})_3N_2.$$

1093. *Cinnamic acid*, $C_9H_8O_2 = C_6H_5.CH{:}CH.CO.OH$, *β-phenyl acrylic acid*, occurs naturally in balsams (storax, Tolu and Peru balsams) and resins (benzoïn), and is formed by the oxidation of its alcohols and ethers, and synthetically by the action of sodium and carbonic anhydride on *α*-brom-styrolene (§ 1042):

$$C_6H_5.CH{:}CHBr + CO_2 + Na_2 = NaBr + C_6H_5.CH{:}CH.CO.ONa;$$

by heating benzaldehyde with chlor-acetal:

$$C_6H_5.CHO + CH_3.CO.Cl = HCl + C_6H_5.CH{:}CH.CO.OH;$$

and by heating benzaldehyde with acetic anhydride and sodic acetate, the reaction in this case not being clearly understood. It can be prepared in largest quantity from storax. This is first heated with soda solution in a distilling vessel, when styrolene distils with the water vapour, whilst the free cinnamic acid goes into solution as sodic salt. The residue containing styracine is then boiled with concentrated solution of sodic hydrate, when styryl alcohol passes over. The filtered solution of sodic salt is then decomposed by hydrochloric acid, the separated cinnamic acid purified by solution in ammonia and reprecipitation and finally distilled.

Cinnamic acid, like benzoic acid, crystallises from boiling water in needles, from alcohol in large, readily cleavable rhombic prisms. It melts at 133°, boils at 290°, and is difficultly soluble in cold water. Its salts resemble those of benzoic acid.

On gentle heating with dilute sulphuric acid and potassic chromate or permanganate it is first converted into benzaldehyde:

$$C_6H_5.CH{:}CH.CO.OH + 4O = C_6H_5.CHO + 2CO_2 + H_2O,$$

and finally into benzoic acid. It unites with nascent hydrogen, forming *β*-phenyl-propionic acid (§ 1074), and is decomposed on heating with lime into carbonic anhydride and styrolene (§ 1042), by fusion with potassic hydrate into benzoic and acetic acids (comp. § 790):

$$C_6H_5.CH{:}CH.CO.OK + HOK + H_2O = C_6H_5.CO.OK$$
$$+ CH_3.CO.OK + H_2.$$

1094. *Ethereal salts of cinnamic acid* are prepared like those of other monobasic acids. *Ethylic cinnamate*, $C_9H_7O.O.C_2H_5$, is an oil boiling at 267°. *Benzylic cinnamate,* $C_9H_7O.O.CH_2.C_6H_5$, or *cinnameïn,* occurs naturally in Tolu and Peru balsams; it crystallises in shining prisms, melts at 39°, and can only be distilled unchanged under reduced pressure. *Cinnamic cinnamate:*

$$C_6H_5.C_2H_2.CO.O.CH_2.C_2H_2.C_6H_5,$$

or *styracine,* is contained in large quantity in storax, and is left as a colourless mass after long digestion with soda solution. It crystallises from ether alcohol in groups of fine needles and melts at 44°.

Cinnamic anhydride, $(C_6H_5.C_2H_2.CO)_2O$, is obtained in colourless crystals by the action of phosphoric oxychloride on sodic cinnamate; it melts at 127° and is nearly insoluble in alcohol. Phosphoric chloride converts cinnamic acid into *chlor-cinnamyl:*

$$C_6H_5.C_2H_2.CO.Cl,$$

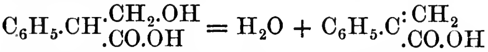
a heavy yellow oil, boiling at 260°–262°. Water slowly converts it into cinnamic and hydrochloric acids; with alcohol it gives ethylic cinnamate, and ammonia gas converts it into *cinnamide:*

$$C_6H_5.C_2H_2.CO.NH_2,$$

a crystalline mass closely resembling benzamide.

Isomers of Cinnamic Acid.

1095. *Atropic* and *isatropic acids* are obtained together by heating tropic acid with baryta or hydrochloric acid, and are therefore also formed in the preparation of tropic acid from atropine. Atropic acid is obtained in largest quantity when baryta is used, whilst hydrochloric acid gives principally isatropic acid. *Atropic acid, α-phenyl acrylic acid,* crystallises in monoclinic tables; it melts at 106°–107°, is moderately soluble in hot water, but requires 700–800 parts of cold water for solution. Its formation is represented by the equation:



$$C_6H_5.CH\genfrac{}{}{0pt}{}{.CH_2.OH}{.CO.OH} = H_2O + C_6H_5.C\genfrac{}{}{0pt}{}{:CH_2}{.CO.OH}$$

It unites with nascent hydrogen, forming α-phenyl-propionic acid (§ 1074); fusion with potassic hydrate converts it into phenyl-acetic and formic acids; chromic acid oxidises it into benzoic acid, carbonic anhydride, and water.

Isatropic acid crystallises in thin rhombic plates, is more difficultly soluble in water than the preceding, melts at 200°, is not oxidised by chromic acid, and does not combine with nascent hydrogen. From these reactions it is probably a polymer (diatropic acid?)

Addition Products of Cinnamic Acid.

1096. Cinnamic acid combines with hydrogen (as already mentioned), the halogens, hydrogen haloids, and hypochlorous acid.

Cinnamic acid dibromide, α-phenyl-dibrom-propionic acid:

$$C_6H_5.CHBr.CHBr.CO.OH,$$

is obtained by addition of bromine to a solution of cinnamic acid in carbonic disulphide; it crystallises in colourless rhombic plates and is insoluble in cold water. On boiling with water it yields partly β-brom-styrolene, carbonic anhydride, and hydrobromic acid:

$$C_6H_5.CHBr.CHBr.CO.OH = C_6H_5.CBr{:}CH_2 + CO_2 + HBr,$$

partly hydrobromic acid and

Phenyl-brom-lactic acid, $C_6H_5.CHBr.CH(OH).CO.OH$, in the form of hexagonal tables containing water of crystallisation; when anhydrous it melts at 125°.

Phenyl-chlor-lactic acid, $C_6H_5.CHCl.CH(OH).CO.OH$, is the addition product of hypochlorous acid with cinnamic acid, and is most readily obtained when a solution of equal molecules of sodic carbonate and cinnamate is saturated with chlorine, the solution of sodic salts acidulated with hydrochloric acid, and after evaporation extracted with ether. The acid crystallises with one molecule of water in hexagonal plates, and then melts at 70°–80°; when anhydrous it melts at 104°.

Aqueous solutions of both phenyl halogen lactic acids are converted by sodium amalgam into phenyl lactic acid.

Substitution Products of Cinnamic Acid.

1097. Two varieties are known, according as the substitution occurs in the C_2H_2 group or in the benzene nucleus. The first includes both the isomeric

Phenyl-brom-acrylic acids:

$$C_6H_5.CH{:}CBr.CO.OH \text{ and } C_6H_5.CBr{:}CH.CO.OH.$$

They are both formed at the same time by the decomposition of cinnamic acid dibromide with alcoholic potassic hydrate, and are separated by aid of their ammonic salts. The acid of the difficultly soluble salt, commonly termed *α-brom-cinnamic acid*, crystallises in long shining needles, melts at 130°–131°, and can be volatilised unchanged, whilst the acid of the more readily soluble salt, *β-brom-cinnamic acid*, crystallises in hexagonal plates, melts at 120°, and is converted into the isomeric α-acid on distillation.

1098. The second variety of substitution products are represented by the nitro-cinnamic acids, the coumaric acids, and their derivatives.

Nitro-cinnamic acids, $C_6H_4(NO_2).C_2H_2.CO.OH$, are formed by the slow addition of cinnamic acid to cold concentrated nitric acid, which must be free from nitrous acid in order to prevent oxidising action.

In order to separate the resulting isomers they are converted into ethylic salts, of which one, ethylic paranitro-cinnamate, is nearly insoluble in alcohol, whilst ethylic orthonitro-cinnamate is readily soluble. By saponification of these bodies and decomposition of the aqueous solutions of the alkali salts with mineral acids the insoluble free nitro-cinnamic acids are obtained. *Paranitro-cinnamic acid* crystallises in fine needles; it melts at 265° and is very difficultly soluble in alcohol. *Orthonitro-cinnamic acid* is more readily soluble in alcohol; it melts at 232°. On oxidation the first is converted into para, the latter into ortho-nitro benzoic acid.

Tin and hydrochloric acid convert the nitro-cinnamic acids into *amido-cinnamic acids*, $C_6H_4(NH_2).C_2H_2.CO.OH$.

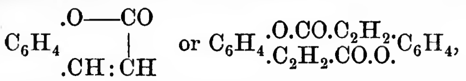
Cinnamic acid dissolves in Nordhausen sulphuric acid, yielding *sulpho-cinnamic acid*, $C_6H_4(SO_2.OH).C_2H_2.CO.OH$, which crystallises in prisms with $3H_2O$. It is readily soluble in water and generally yields soluble salts.

Hydroxy-Cinnamic Acids.

1099. *Monhydroxy-cinnamic acids*, $C_6H_4\begin{array}{l}.OH\\.C_2H_2.CO.OH\end{array}$.

1. *Coumaric acid*, or orthohydroxy-cinnamic acid, occurs, together with hydro-coumaric acid, in *Melilotus officinalis*, and is readily obtained by boiling coumarine with alkalies. It crystallises in colourless prisms, readily soluble in alcohol and hot water; it melts at 195° and is decomposed into potassic acetate and salicylate on heating with potassic hydrate. Its alkali salts show a fine fluorescence in aqueous solution. Ferric chloride gives no violet colour with it.

Coumarine, $C_9H_6O_2$, an ethereal anhydride of coumaric acid:

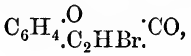


$$C_6H_4\begin{array}{l}.O\text{——}CO\\ \qquad\quad |\\ .CH:CH\end{array} \quad \text{or } C_6H_4\begin{array}{l}.O.CO.C_2H_2.\\.C_2H_2.CO.O.\end{array}C_6H_4,$$

corresponding to lactide and salicylide (§ 1062), occurs in *Asperula odorata*, *Melilotus officinalis*, *Anthoxanthum odoratum*, and especially in tonka beans, the fruit of *Dipterix odorata*, in the latter frequently in fine crystals. It is extracted by alcohol, and after evaporation of the greater part of the solvent separated by addition of water and cooling. It crystallises in colourless prisms of very agreeable odour, is difficultly soluble in cold water; it melts at 67° and boils at 290°. It unites with chlorine and bromine, forming dihaloids, e.g.

$$C_9H_6Br_2O_2,$$

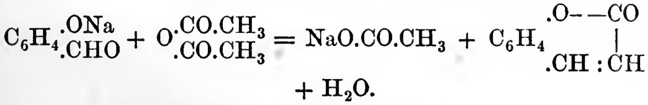
which on heating yield halogen-substituted coumarines:



$$C_6H_4\begin{array}{l}.O\\.C_2HBr.\end{array}CO,$$

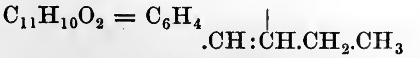
or (by also uniting with water) the respective coumaric acids.

The synthesis of coumarine and its homologues (which latter do not occur naturally) by heating sodium salicylic aldehyde (§ 1033) with the anhydrides of the acetic series is very interesting. Acetic anhydride so treated gives coumarine:



$$C_6H_4\begin{array}{l}.ONa\\.CHO\end{array} + O\begin{array}{l}.CO.CH_3\\.CO.CH_3\end{array} = NaO.CO.CH_3 + C_6H_4\begin{array}{l}.O\text{——}CO\\ \qquad\quad |\\ .CH:CH\end{array} + H_2O.$$

Butyric anhydride gives a body melting at 70°–71° and boiling at 296°, probably ethyl coumarine:

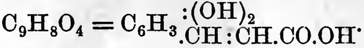


$$C_{11}H_{10}O_2 = C_6H_4\begin{array}{l}.O\ .\ CO\\ \qquad\quad |\\ .CH:CH.CH_2.CH_3\end{array}$$

Isovaleric anhydride gives a compound $C_{12}H_{12}O_2$, forming long prisms, melting at 54° and boiling at 301°, probably isopropyl coumarine, &c.

2. *Paracoumaric acid,* or *parahydroxy-cinnamic acid,* isomeric with coumaric acid, is obtained by boiling a solution of aloes acidulated with dilute sulphuric acid, and withdrawn from the filtered liquid by shaking with ether. It crystallises in brittle needles, readily soluble in hot water and alcohol, and melts at 179°–180°. It unites with nascent hydrogen, forming hydro-paracoumaric acid (§ 1083, 3), and gives acetate and paraoxy-benzoate on fusion with potassic hydrate.

Only one dihydroxy-cinnamic acid is yet known.



Caffeic acid, $C_9H_8O_4 = C_6H_3\begin{matrix}:(OH)_2\\ .CH:CH.CO.OH\end{matrix}$. It is obtained from extract of coffee by boiling with potassic hydrate and addition of sulphuric acid; it forms yellowish prisms and plates scarcely soluble in cold water, more readily in hot water, and is very soluble in alcohol and ether. Ferric chloride gives a grass-green coloration, changing to red on addition of soda. On dry distillation it yields pyrocatechin amongst other products; fusion with potassic hydrate converts it into potassic acetate and protocatechuate :

$$C_6H_3(OH)_2.CH:CH.CO.OK + HOK + H_2O = H_2 \\ + C_6H_3(OH)_2.CO.OK + CH_3.CO.OK.$$

It unites with nascent hydrogen, forming hydrocaffeic acid.

Caffetannic acid, a glucoside, accompanies caffeic acid in coffee extract; it can be precipitated from the alcoholic extract by plumbic acetate, and the resulting precipitate suspended in water and decomposed with sulphuretted hydrogen. The filtrate on evaporation yields a yellowish gummy mass of the acid. Its solutions are coloured green by ferric chloride, and on boiling with potassic hydrate split up into caffeic acid and an amorphous sugar-like substance. Its solution in lime water readily absorbs oxygen, becoming first a fine green, then blue, and finally brown.

1100. The following bodies also appear to belong to the cinnamic group :—

Anethol, $C_{10}H_{12}O$, is contained in the oils of anise, fennel, star anise, &c., and crystallises out when the temperature is lowered. After pressing and recrystallisation from ether it forms colourless shining prisms, melting at 21° and boiling at 232°, sp. gr. 1·014. It unites with hydrochloric acid, forming a liquid compound :

$$C_{10}H_{13}ClO.$$

Potassic hydrate at 200° decomposes anethol into para-oxybenzoic acid and anol, $C_9H_{10}O$. This latter is a phenol-like body, crystallising in white plates, melting at 92·5°. Boiling dilute nitric acid oxidises anethol to anisic aldehyde (§ 1033); chromic and sulphuric acids oxidise it to anisic acid (§ 1065). In both cases oxalic and carbonic acids are also formed. Concentrated sulphuric acid, phosphoric acid, zincic chloride, and iodine convert it into isomeric or polymeric modifications.

From these reactions the formula for anethol is probably :

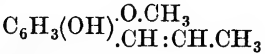
$$CH_3.O.C_6H_4.C_3H_5 \ (1:4),$$

in which, however, the constitution of the C_3H_5 group still remains uncertain.

1101. *Eugenol*, $C_{10}H_{12}O_2$, isomeric with cumic acid, is contained in the ethereal oils of *Eugenia caryophyllata, Myrtus pimenta, Persea caryophyllata*, and *Canella alba*, from which it can be extracted by shaking with potassic hydrate and obtained in a state of purity by precipitating the clear solution with carbonic anhydride. It is a colourless oil of aromatic odour; it boils at 253° and has sp. gr. 1·068 at 14°. The potassic compound has the formula $C_{10}H_{11}KO_2$; the baric compound, $(C_{10}H_{11}O_2)_2Ba$, forms difficultly soluble nacreous plates. Treated with chlor-acetyl and chlor-benzoyl it gives acetyl and benzoyl derivatives. *Benzoyl eugenol*, $C_{10}H_{11}O_2.C_7H_5O$, forms colourless needles melting at 50°. Hydriodic acid decomposes eugenol into methylic iodide and a red resin, $C_9H_{10}O_2$:

$$H_{10}H_{12}O_2 + HI = CH_3I + C_9H_{10}O_2.$$

Fusion with potassic hydrate converts it into protocatechuic acid, acetic acid, carbonic anhydride, and hydrogen. From these reactions the formula



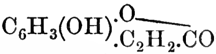
$$C_6H_3(OH)\begin{matrix}.O.CH_3\\ .CH:CH.CH_3\end{matrix}$$

may be assigned to eugenol.

By the action of sodium and carbonic anhydride eugenol is converted into the sodic salt of *eugetinic acid* :

$$C_6H_3\left\{\begin{array}{l}OH\\ O.CH_3\\ C_3H_5\end{array}\right. + Na_2 + CO_2 = C_6H_2\left\{\begin{array}{l}ONa\\ O.CH_3\\ C_3H_5\\ CO.ONa\end{array}\right. + H_2$$

from whose solution eugetinic acid is precipitated by hydrochloric acid. It forms colourless prisms, melts at 124°, and is difficultly soluble in water. At higher temperatures it again decomposes into carbonic anhydride and eugenol; with ferric chloride it gives a deep blue coloration.



1102. *Umbelliferone*, $C_9H_6O_3 = C_6H_3(OH)\begin{matrix}.O\text{———}\\ .C_2H_2.CO\end{matrix}$, occurs amongst the products of the dry distillation of galbanum and the resins from other umbelliferæ; it crystallises in rhombic prisms, melts at 240°, and dissolves with difficulty in water, the solution having a blue fluorescence. Treated with chlor-acetyl it gives a *monacetate*, $C_9H_5(C_2H_3O)O_3$; with sodium amalgam and water, the sodic salt of umbellic acid (§ 1088).

1103. *Homologues of Cinnamic Acid.*—These bodies are all prepared by heating benzaldehyde or cumic aldehyde with an anhydride of an acid of the acetic series, the sodic salt of the same acid being present. The acids so far obtained are given below.

Phenyl crotonic acid, $C_{10}H_{10}O_2 = C_6H_5.C_3H_4.CO.OH$, m.p. 78°.

Isophenyl crotonic acid, $C_{10}H_{10}O_2$, m.p. 83°–84°.

Phenyl angelic acid, $C_{11}H_{12}O_2 = C_6H_5.C_4H_6.CO.OH$, m.p. 105°–106°.

Cumenyl acrylic acid, $C_{12}H_{14}O_2 = C_6H_4(C_3H_7).C_2H_2.CO.OH$, m.p. 157°–158°.

Cumenyl crotonic acid, $C_{13}H_{16}O_2 = C_6H_4(C_3H_7).C_3H_4.CO.OH$, m.p. 90°–91°.

Cumenyl angelic acid, $C_{14}H_{18}O_2 = C_6H_4(C_3H_7).C_4H_6.CO.OH$, m.p. 123°.

Phenyl Propiolic Acid, $C_9H_6O_2$.

1104. Phenyl propiolic acid stands in the same relation to phenyl propionic and cinnamic acids as the acids of the $C_nH_{2n-4}O_2$ series (§ 854) to the fatty acids $C_nH_{2n}O_2$ and the members of the acrylic acid series.

It is prepared synthetically by the action of sodium and carbonic anhydride on β-brom-styrolene:

$$C_6H_5.CBr{:}CH_2 + Na_2 + CO_2 = C_6H_5.C\vdots C.CO.ONa + NaBr + H_2,$$

and by the direct union of sodium phenyl acetylene (§ 1042) with carbonic anhydride:

$$C_6H_5.C\vdots CNa + CO_2 = C_6H_5.C\vdots C.CO.ONa.$$

It is further obtained by heating α-brom-cinnamic acid with alcoholic potassic hydrate:

$$C_6H_5.C_2HBr.CO.OK + KOH = KBr + H_2O \\ + C_6H_5.C\vdots C.CO.OK.$$

It crystallises in colourless, volatile needles, melts between 136° and 137°, and is readily soluble in alcohol, ether, and hot water. Heated with water at 120° it splits up into carbonic anhydride and phenyl acetylene:

$$C_6H_5.C\vdots C.CO.OH = CO_2 + C_6H_5.C\vdots CH.$$

It unites directly with four atoms of bromine, forming

$$C_6H_5.CBr_2.CBr_2.CO.OH,$$

and with four atoms of nascent hydrogen yielding phenyl propionic acid. Chromic acid oxidises it to benzoic acid.

POLYBASIC AROMATIC ACIDS.

1105. The polybasic aromatic acids contain several acid groups, CO.OH, united to the benzene nucleus, either directly or by means of a hydrocarbon group. Their general properties, reactions, and methods of preparation correspond to those of the monobasic acids, but they unite more readily with nascent hydrogen with formation of additive products.

DIBASIC ACIDS.

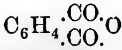
Phenylene Dicarbonic Acids, $C_8H_6O_4 = C_6H_4(CO.OH)_2$.

1106. The three isomeric phenylene dicarbonic acids have already been referred to (§ 954) in reference to the aid afforded by them in determining the constitution of the isomeric disubstituted benzene derivatives. Their calcic salts all yield benzene when submitted to dry distillation with lime.

1107. *Phthalic acid*, or *orthophenylene dicarbonic acid*, (1:2), is formed by the oxidation of anthracene and many of its derivatives, also from several bodies derived from anthracene—such as alizarine and purpurine—by oxidation with nitric acid, or manganic dioxide and sulphuric acid, and in small quantities by the action of the latter on benzene or benzoic acid. It crystallises in shining colourless tables or prisms, is readily soluble in hot water, alcohol, and ether, melts at 182°, and at higher temperatures decomposes into water and phthalic anhydride, which volatilise. On heating with hydriodic acid it yields carbonic anhydride and benzoic acid:

$$C_6H_4(CO.OH)_2 = CO_2 + C_6H_5.CO.OH.$$

Benzoic acid is also obtained on heating two molecules of calcic phthalate with one molecule of lime at 330°–350°. Phthalic acid forms hydric and normal salts; they are crystalline and, with the exception of the alkali salts, difficultly soluble in water. The baric salt, $C_6H_4(CO.O)_2Ba$, crystallises in plates. Dimethylic and diethylic phthalates are obtained by saturation of solutions of the acid in the respective alcohols, are both colourless oily liquids which can be distilled.



Phthalic anhydride, $C_8H_4O_3 = C_6H_4\begin{array}{l}.CO.\\ .CO.\end{array}O$, is formed directly by subliming phthalic acid, and also by treating phthalic acid with one molecule of phosphoric chloride (comp. § 835). It crystallises in long shining needles, melts at 127°–128°, and boils at 277°. It dissolves unaltered in alcohol and ether; in boiling water it is slowly converted into phthalic acid. By action of two molecules of phosphoric chloride on phthalic acid

Phthalyl chloride, $C_8H_4O_2Cl_2 = C_6H_4(CO.Cl)_2$, is obtained as a yellow oil, boiling at 270°. On treatment with water it is slowly converted into hydrochloric and phthalic acids; with alcohols it yields ethereal phthalates, and with phenol it gives *phenyl phthalate*:

$$C_6H_4(CO.O.C_6H_5)_2,$$

forming prisms melting at 61° and difficultly soluble in cold alcohol.

Chlor-phthalic acids are obtained by the oxidation of chlor-naphthalenes with dilute nitric acid. *Dichlor-phthalic acid*:

$$C_6H_2Cl_2(CO.OH)_2,$$

prepared from dichlor-naphthalene tetrachloride, forms yellow prisms, melts at 183°–185°, and is moderately soluble in water. *Tetrachlor-phthalic acid*, $C_6Cl_4(CO.OH)_2$, obtained by oxidation of pentachlor-naphthalene, crystallises in leaves and tables, and melts at 250°. On heating these acids decompose into water and chlor-anhydrides, in the latter case even on fusing.

On heating phthalic acid with nitro-sulphuric acid, *nitro-phthalic acid*, $C_6H_3(NO_2)(CO.OH)_2$, is obtained in the form of yellow prisms, melting at 212° and moderately soluble in water; on treatment with tin and hydrochloric acid, carbonic anhydride is eliminated and met-amido-benzoic acid formed.

1108. *Hydrophthalic Acids.—Dihydrophthalic acid*:

$$C_8H_8O_4 = C_6H_6(CO.OH)_2,$$

is formed by the long-continued action of sodium amalgam on a cold solution of sodic phthalate, and is separated on addition of hydrochloric acid. It crystallises in plates and tables, is difficultly soluble in cold water and ether, readily in boiling water and alcohol. It fuses at 200° with decomposition into hydrogen, water, and phthalic anhydride. Its easy convertibility into benzoic acid and its derivatives is peculiar to it. This occurs on addition of bromine to an aqueous solution:

$$C_6H_6(CO.OH)_2 + Br_2 = C_6H_5.CO.OH + CO_2 + 2HBr,$$

or on oxidation with dilute nitric acid. Phosphoric chloride converts it into chlor-benzoyl and carbon monoxide:

$$C_6H_6(CO.OH)_2 + 2PCl_5 = C_6H_5.CO.Cl + CO + 2POCl_3 + 3HCl.$$

On saturating alcoholic solutions of the acid with hydrochloric acid the corresponding ethereal benzoates are formed.

Tetrahydrophthalic acid, $C_8H_{10}O_4 = C_6H_8(CO.OH)_2$, is obtained by dry distillation of isohydropyromellitic acid, first as the *anhydride*, $C_6H_8(CO)_2O$, crystallising in plates and melting at 86°, which on treatment with water is converted into the acid. This crystallises in plates, melts at 96°, but already at this temperature decomposes into water and the anhydride. *Hexahydrophthalic acid*, $C_6H_{10}(CO.OH)_2$, is obtained from both the preceding by heating at 230° with concentrated hydriodic acid, and also from tetrahydrophthalic acid by treatment with sodium amalgam. It melts at 207°, is difficultly soluble in water, and crystallises in plates or prisms.

1109. *Isophthalic acid,* or *metaphenylene dicarbonic acid,* (1:3), is obtained by oxidation of metaxylene and metatoluic acid with chromic and sulphuric acids, by fusion of potassic metasulpho-benzoate with potassic formate, and finally as ethylic salt by the action of ethylic chloro-carbonate and sodium on that dibrom-benzene which yields three isomeric tri-derivatives on further substitution, and which must therefore have the bromine atoms in the meta position:

$$C_6H_4Br_2 + 2Cl.CO.C_2H_5 + 2Na_2 = 2NaBr$$
$$+ 2NaCl + C_6H_4(CO.O.C_2H_5)_2.$$

It crystallises in hair-like prisms, difficultly soluble even in boiling water; it melts above 300° and sublimes. Its salts are in part more readily soluble than those of phthalic acid, e.g. *baric isophthalate,* $C_6H_4(CO.O)_2Ba,3H_2O$.

Phosphoric pentachloride converts it into *isophthalic chloride,* $C_6H_4(COCl)_2$, a fibro-crystalline mass, melting at 41° and boiling at 276°, which reacts on phenol, forming *phenyl isophthalate:*

$$C_6H_4(CO.O.C_6H_5)_2,$$

in form of needles, melting at 120° and dissolving with difficulty in hot alcohol.

Methylic isophthalate, $C_6H_4(CO.O.CH_3)_2$, is also crystalline, and melts at 65°. *Ethylic isophthalate,* $C_6H_4(CO.O.C_2H_5)_2$, is an oil which solidifies at 0° and boils at 285°.

Concentrated nitric acid converts isophthalic acid into *nitro-isophthalic acid,* $C_6H_3(NO_2)(CO.OH)_2$, forming thin plates, melting at 248°–249°, and reduced by tin and hydrochloric acid to *amido-isophthalic acid,* $C_6H_3(NH_2)(CO.OH)_2$, crystallising in difficultly soluble plates, melting at 300°.

1110. *Terephthalic acid,* or *paraphenylene dicarbonic acid,* is formed from paradialkyl benzenes, paratoluic acid, cuminol, cumic acid, &c., by oxidation with chromic and sulphuric acids; it can be obtained from that dibrom-benzene which only yields a single tri-derivative on further substitution (and in which therefore the bromine atoms must be in the para position) by treatment with sodium and methylic iodide, when paraxylene is obtained, which on oxidation yields terephthalic acid. Terephthalic acid can also be obtained from potassic benzene-paradisulphonate. This on dry distillation with potassic cyanide gives *paraphenylene dicyanide,* $C_6H_4(CN)_2$, and this on saponification yields a salt of terephthalic acid. It forms a white crystalline powder, nearly insoluble in water, alcohol, and ether, and sublimes without previous fusion above 300°. The baric salt, $C_6H_4(CO.O)_2Ba,4H_2O$, is very difficultly soluble. The *methylic* and *ethylic salts* both crystallise in prisms; the first melts at 144°, the latter at 44°.

Terephthalyl chloride, $C_6H_4(CO.Cl)_2$, prepared by aid of phosphoric chloride, melts at 78°. *Phenylic terephthalate* melts at 191°, and crystallises in needles very difficultly soluble in boiling water. *Nitro-terephthalic acid,* $C_6H_3(NO_2)(CO.OH)_2$, obtained by boiling terephthalic acid with concentrated nitric acid, is moderately soluble in water, crystallises in cauliflower-like masses, and melts at 259°.

After long treatment of an alkaline terephthalic acid solution with sodium amalgam addition of hydrochloric acid precipitates a white powder, consisting of *dihydro-terephthalic acid*, $C_6H_6(CO.OH)_2$.

Homologues of Phenylene Dicarbonic Acids.

Acids of the Formula $C_9H_8O_4$.

1111. 1. *Uvitic acid:*

$$C_6H_3(CH_3)(CO.OH)_2 \quad [CO.OH:CH_3:CO.OH = 1:3:5],$$

was first obtained by boiling pyroracemic acid with excess of baryta water:

$$3C_3H_4O_2 + Ba(OH)_2 = C_9H_6BaO_4 + 4H_2O,$$

and later by oxidation of mesitylene (§ 1024, 1) with dilute nitric acid, mesitylenic acid being also formed. It dissolves with difficulty in hot water, more readily in alcohol and ether, and crystallises in fine needles melting at 287°. On heating with lime at 350° it yields calcic carbonate and metatoluate (§ 1073, 2); at higher temperatures it gives toluene.

2. *Xylidic acid:*

$$C_6H_3(CH_3)(CO.OH)_2 \quad [CO.OH:CH_3:CO.OH = 1:3:4],$$

is obtained by oxidation of pseudo-cumene (§ 1024, 2), xylic acid, and paraxylic acid (§ 1076) with dilute nitric acid. It forms colourless crystals, melts at 280°–283°, and is difficultly soluble in cold water.

3. *Isoxylidic acid* is also a benzene methyl dicarbonic acid, and is prepared by fusing potassic toluene disulphonate with sodic formate:

$$C_6H_3(CH_3)(SO_2.OK)_2 + 2H.CO.OK = 2SO_3K_2 \\ + C_6H_3(CH_3)(CO.OH)_2.$$

It resembles xylidic acid very closely, but melts at 310°–315°.

4. *Isouvitic acid* is formed from gamboge by fusion with potassic hydrate, phloro-glucine, pyrotartaric acid, and acetic acid being formed at the same time. It crystallises in short rhombic prisms, melts at 160°, and is readily soluble in boiling water.

Acids of the Formula $C_{10}H_{10}O_4$.

1112. 1. *Cumidic acid*, $C_6H_2(CH_3)_2(CO.OH)_2$, is obtained by long-continued boiling of durene (§ 1025) or durylic acid with dilute nitric acid. It crystallises from boiling alcohol in long shining prisms, is nearly insoluble in boiling water, and sublimes in tables without previous fusion.

2. *Paraphenylene diacetic acid*, $C_6H_4(CH_2.CO.OH)_2$. Tollylene dibromide (§ 1041), when heated with alcoholic solution of potassic cyanide, yields *tollylene dicyanide*, $C_6H_4(CH_2.CN)_2$, melting between 88°–90°. This is then heated with alcoholic potassic hydrate as long as ammonia is evolved, and acid added to the aqueous solution of the potassic salt formed. The free acid so obtained forms indistinct crystals; it is nearly insoluble in water and melts at 236°.

1112*a*. *Phenol dicarbonic acid*, $C_8H_6O_5 = C_6H_3(OH)(CO.OH)_2$, is prepared by heating basic sodic salicylate at 360°–380° in carbonic anhydride. The free acid crystallises in needles, melts at above 270°, and can be sublimed with partial decomposition.

Oxyisouvitic acid, $C_9H_8O_5 = C_6H_2(OH)(O.CH_3)(CO.OH)_2$, is obtained as its ethylic salt by the action of ethylic aceto-acetate upon chloroform. The free acid crystallises in needles.

Hemipinic acid, $C_{10}H_{10}O_6 = C_6H_2(O.CH_3)_2(CO.OH)_2$, will be noticed in connection with the opium alkaloids (§ 1265).

TRIBASIC ACIDS, $C_9H_6O_6 = C_6H_3(CO.OH)_3$.

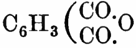
1113. Only one of the three isomeric acids of this formula (trimesic acid) can be obtained by the oxidation of a trimethyl benzene.

1. *Trimesic acid*, (1:3:5), is obtained by the oxidation of mesitylene, mesitylenic acid, and uvitic acid by chromic and sulphuric acids, from mellitic acid by heating with glycerine in an oil bath until the whole mass has become solid:

$$C_6(CO.OH)_6 = 3CO_2 + C_6H_3(CO.OH)_3,$$

and together with the tetrabasic prehnitic and mellophanic acids from the isomeric hexahydromellitic acids by heating with sulphuric acid. It crystallises in prisms, melts at above 300°, can be sublimed, is difficultly soluble in cold water, and gives benzene on distillation with excess of lime.

2. *Trimellitic acid*, (1:2:4). Hydropyromellitic acid, on heating with concentrated sulphuric acid, yields isophthalic and trimellitic acids, which can be separated by aid of the different solubility of their baric salts (that of trimellitic acid, $(C_9H_3O_6)_2Ba_3,3H_2O$, being very difficultly soluble). Trimellitic acid crystallises in warty masses, is moderately soluble in water and ether, melts at 216°, and on long heating at this temperature is converted into water and *anhydrotrimellitic acid*, $C_6H_3\left(\begin{matrix}CO.\\CO.\end{matrix}O\right).CO.OH$. It also occurs amongst the products of the oxidation of colophony by nitric acid.



$$C_6H_3\left(\begin{matrix}CO.\\CO.\end{matrix}O\right).CO.OH$$

3. *Hemimellitic Acid.*—On heating with sulphuric acid, hydromellophanic acid yields phthalic anhydride and hemimellitic acid. It crystallises in colourless needles, is difficultly soluble in water, melts at 185°, and then decomposes into phthalic anhydride, benzoic acid, and carbonic anhydride.

1113*a*. *Phenol tricarbonic acid*, $C_9H_6O_7 = C_6H_2(OH)(CO.OH)_3$, is obtained, together with phenol dicarbonic acid, by the action of carbonic anhydride on basic sodic salicylate. It crystallises in thick prisms containing one molecule of water of crystallisation; it decomposes at 180°.

TETRABASIC ACIDS, $C_{10}H_6O_8 = C_6H_2(CO.OH)_4$.

1114. All three possible benzene tetracarbonic acids are known, and are all derived from mellitic acid.

1. *Pyromellitic acid*, (1:2:4:5 or 1:2:5:6). Pyromellitic anhydride is the chief product of the dry distillation of mellitic acid, and is obtained most abundantly when sodic mellitate is distilled with 1½ time its weight of sulphuric acid. On recrystallising from water the acid is obtained in colourless prisms of the formula

$$C_6H_2(CO.OH)_4,2H_2O.$$

It dissolves to a large extent in hot water and alcohol. When anhydrous it melts at 240° and decomposes again into water and pyromellitic anhydride, $C_6H_2\left\{\begin{array}{l}\left.\begin{array}{l}CO.\\CO.\end{array}\right\rangle O\\ \left.\begin{array}{l}CO.\\CO.\end{array}\right\rangle O\end{array}\right.$. This latter melts at 286°, and on distillation solidifies to a mass of large crystals. Phosphoric chloride converts pyromellitic acid into the anhydrochloride:

$$C_6H_2\left\{\begin{array}{l}(CO)_2O\\(COCl)_2\end{array}\right.$$

and the chloride, $C_6H_2(COCl)_4$, both crystalline compounds. Ethylic pyromellitate, $C_6H_2(CO.O.C_2H_5)_4$, is obtained by heating argentic pyromellitate with ethylic iodide at 100°, crystallises from alcohol in short, flat needles, melting at 53°.

By the action of sodium amalgam, continued for several weeks, on pyromellitic acid, two isomeric *tetrahydro-pyromellitic acids:*

$$C_{10}H_{10}O_8 = C_6H_6(CO.OH)_4,$$

are obtained—*hydro-pyromellitic acid,* which is amorphous, and *isohydro-pyromellitic acid*—crystallising with two molecules of water in grouped needles. It loses its water of crystallisation at 120°, and melts above 200° with decomposition into carbonic anhydride, water, and tetrahydro-phthalic anhydride. On heating with concentrated sulphuric acid it is in part converted into pyromellitic anhydride:

$$C_6H_6(CO.OH)_4 + 2H_2SO_4 = 2SO_2 + 6H_2O + C_6H_2\left\{\begin{array}{l}(CO)_2O\\(CO)_2O\end{array}\right.$$

and partly into carbonic anhydride, trimellitic acid, and isophthalic acid.

On heating hydromellitic acid with five times its weight of concentrated sulphuric acid in a retort, until one-half of the sulphuric acid has distilled, the hydromellitic acid is decomposed, with evolution of carbonic and sulphurous anhydrides and water, into trimesic acid, prehnomalic acid, and both the tetrabasic acids, *prehnitic* and *mellophanic acids,* both of which are readily soluble in water, and may be separated in the form of their baric salts, of which that of prehnitic acid is difficultly soluble.

2. *Prehnitic acid,* (1:2:3:5), crystallises in large prisms united in groups, of the formula $C_{10}H_6O_8,2H_2O$. When anhydrous it melts at 240° and decomposes into water and *anhydro-prehnitic acid:*

$$C_6H_2\left\{\begin{array}{l}(CO)_2O\\(CO.OH)_2\end{array}\right.$$

By long-continued action of sodium amalgam on its aqueous solution prehnitic acid is converted into *hydroprehnitic acid,* $C_6H_6(CO.OH)_4$; on heating with strong sulphuric acid this decomposes into prehnitic acid, carbonic anhydride, and isophthalic acid.

3. *Mellophanic acid* forms anhydrous crystalline crusts, melts between 215° and 238°, and yields a hydro-acid on treatment with nascent hydrogen.

Hexabasic Acid, $C_{12}H_6O_{12} = C_6(CO.OH)_6$.

1115. *Mellitic acid* occurs as aluminic salt in *mellite* or *honeystone*, a rare mineral crystallising in yellow quadratic pyramids and occurring in lignite. On boiling mellite with ammonic carbonate alumina separates, and on evaporation the solution yields large rhombic prisms of *ammonic mellitate*, $C_6(CO.O.NH_4)_6,9H_2O$, which by precipitation with baric chloride are converted into the difficultly soluble crystalline baric salt $C_6[(CO.O)_2Ba]_3,3H_2O$. By decomposition of this latter with the requisite quantity of sulphuric acid mellitic acid is obtained in the free state.

It crystallises in fine silky needles, readily soluble in water and alcohol. On heating alone it yields pyromellitic anhydride:

$$C_6(CO.OH)_6 = 2CO_2 + 2H_2O + C_6H_2[(CO)_2O]_2.$$

Heated with glycerine it gives trimesic acid:

$$C_6(CO.OH)_6 = 3CO_2 + C_6H_3(CO.OH)_3;$$

and distilled with excess of lime it yields benzene:

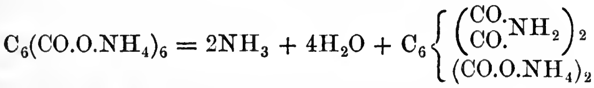
$$C_6(CO.OH)_6 + 6CaO = 6CaCO_3 + C_6H_6.$$

Nitric acid, hydriodic acid, and bromine do not alter it even at high temperatures.

It has been prepared artificially by the oxidation of pure wood charcoal with an alkaline solution of potassic permanganate.

Ammonic mellitate decomposes at 160° into ammonia water, ammonic euchroate, and mellimide.

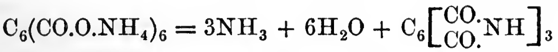
Ammonic euchroate is formed according to the equation:



$$C_6(CO.O.NH_4)_6 = 2NH_3 + 4H_2O + C_6\left\{\begin{array}{l}\left(\begin{array}{l}CO.\\CO.\end{array}NH_2\right)_2\\(CO.O.NH_4)_2\end{array}\right.$$

On acidulating its aqueous solution *euchroic acid*, $C_{12}N_2H_4O_8$, separates in short colourless prisms, difficultly soluble in cold water. The aqueous solution, on treatment with nascent hydrogen, gives an insoluble deep blue precipitate, *euchrone*, which again oxidises to euchroic acid on exposure to air.

Mellimide, or *paramide*, is formed according to the equation:



$$C_6(CO.O.NH_4)_6 = 3NH_3 + 6H_2O + C_6\left[\begin{array}{l}CO.\\CO.\end{array}NH\right]_3$$

It is a white amorphous mass, insoluble in water and alcohol; on heating with water at 200° it is converted into acid ammonic mellitate.

Long-continued action of sodium amalgam on aqueous ammonic mellitate converts it into sodic hydromellitate. The solution gives with plumbic acetate a precipitate of plumbic mellitate, which on decomposition with sulphuretted hydrogen yields *hydromellitic acid*:

$$C_6H_6(CO.OH)_6.$$

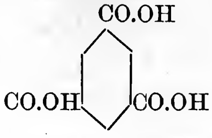
It remains on evaporation as an indistinctly crystalline mass. On keeping, or rapidly on heating at 180°, it is converted into the isomeric *isohydromellitic acid,* forming hard tetragonal prisms, soluble in water, but insoluble in hydrochloric acid. Both hydromellitic acids, on heating with sulphuric acid, yield trimesic, prehnitic, and mellophanic acids.

Constitution of the Tri- and Tetra-basic Acids.

1116. According to the benzene theory at present accepted the acids $C_6H_3(CO.OH)_3$ and $C_6H_2(CO.OH)_4$ can each exist in three isomeric modifications, all of which are known.

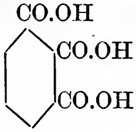
In determining their constitution the formation of trimesic acid from mesitylene leads to the formula:

(1)

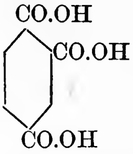


leaving for the other two isomers the expressions:

2)



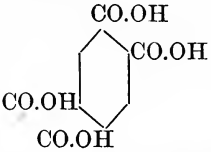
(3)



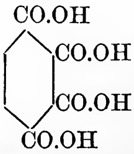
of which the (2) = 1:2:3 probably belongs to hemimellitic acid, as it decomposes into carbonic anhydride, water, and phthalic anhydride on heating, leaving (3) = 1:2:4 for trimellitic acid, which on heating yields only water and anhydromellitic acid.

With regard to the three tetrabasic acids the most important evidence is given by the formation of their anhydrides. As in the case of the dibasic acids, only the ortho compound, phthalic acid, gives such a body, it is probable that anhydride formation depends on the neighbouring position of the CO.OH groups. Two of the tetrabasic acids, namely

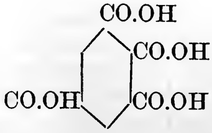
(1)



(2)



could yield, like pyromellitic acid, a double anhydride. The third possible isomer:



on the contrary, would only yield anhydro-acids, thus agreeing with prehnitic acid. The formula (1) or (2) cannot as yet be decidedly assigned to pyromellitic and mellophanic acids respectively, but the symmetrical expression (1) probably corresponds to pyromellitic acid, as that is obtained directly from mellitic acid.

The constitution of mellitic acid admits of no doubt; the formation of two isomeric hexahydromellitic acids only necessitates the view that the hydromellitic acid first formed,  $\left(\mathrm{C}\begin{matrix}.\mathrm{H}\\ .\mathrm{CO.OH}\end{matrix}\right)_6$, during its conversion into the iso-acid exchanges hydrogen atoms and CO.OH groups in such a way that some of the carbon atoms of the benzene ring are in union with two CO.OH groups, and as many others united to two hydrogen atoms.

FURTHER SIMPLE BENZENE DERIVATIVES.

1117. There are still some groups of compounds to be described in addition to the simple benzene derivatives already mentioned, which essentially stand in genetic relation to the latter, i.e. which are derived from a closed ring of six carbon atoms. The constitution of these bodies has, however, as yet not been made out with sufficient clearness.

TERPENES, $C_{10}H_{16}$.

1118. The hydrocarbons of the formula $C_{10}H_{16}$, to which the general name of terpenes has been applied, occur either ready-formed in the essential oils of plants or are derived from these natural terpenes by chemical reactions. They are known in numerous isomeric modifications, in a large part of which the isomerism appears to be only physical (§ 47); polymeric modifications are also known. Those best investigated stand in near relation to cymene, $C_{10}H_{14}$ (§ 1023), into which they can be converted in various ways—for instance, by heating with iodine, when hydrogen is eliminated. They are therefore *dihydro-cymenes*, $C_6H_6\begin{matrix}.CH_3\\.C_3H_7\end{matrix}$, one of the double carbon unions in the benzene nucleus having been converted into monovalent, the other two double unions still remaining unchanged. This theory of the constitution of the terpenes agrees with their union with halogens, hydro-acids, water, &c., to form additive products, from which either cymenes or the terpenes themselves can be again obtained.

The boiling points of the terpenes lie between 155° and 175°, their sp. gr. between ·85 and ·88. Many of them can be distinguished by their power of rotating a beam of polarised light in different directions, whilst others are quite inactive.

Oil of Turpentine.

1119. *Turpentine*, a viscous liquid which flows from incisions made in the bark of various coniferæ (especially from *Pinus*, *Abies*, and *Larix*), is a solution of a resin in oil of turpentine. On distilling turpentine with water, the oil passes over, whilst the resin remains behind and on fusion is obtained in the form of *colophony*.

The turpentine oils floating on the top of the aqueous distillate possess different optical rotary powers, according to the source from whence obtained. Most—for instance, that obtained from *Pinus maritima* (French oil of turpentine)—are lævorotary; that from *Pinus australis* (English turpentine oil) is dextrorotary.

Oil of turpentine occurring in commerce is invariably impure, as when exposed to light it readily absorbs atmospheric oxygen, being converted into resin. In order to purify it it is first shaken with solutions of alkaline carbonates, in order to remove free acids (especially formic and acetic acids), and is then purified by distillation in vacuo.

The pure turpentine oils so obtained—*terebenthene*, from *Pinus maritima*, and *australene*, from *Pinus australis*—are mobile, colourless liquids of peculiar odour; they boil at 156°, have sp. gr. ·864 at 15° and a vapour density of 4·698. They are nearly insoluble in water, but impart their odour when shaken with it; they mix in every proportion with alcohol, ether, and acetic acid. They burn with a strongly smoky luminous flame, and are good solvents for sulphur, phosphorus, fats, resins, and many other bodies insoluble in water. Repeated distillation at ordinary atmospheric pressure converts them into isomeric and polymeric modifications of higher boiling points. This change occurs more quickly on heating at 250° in closed vessels. One of the polymers, *metaterebenthene*, boils at 360° and has the formula $C_{20}H_{32}$.

On repeatedly distilling terebenthene with small quantities of concentrated sulphuric acid until a distillate is obtained which is completely optically inactive, *terebene* is obtained; it is a liquid of thyme-like odour, boils at 156°, and unites with two atoms of bromine, and on then boiling with alcoholic potassic hydrate yields cymene:

$$C_{10}H_{16}Br_2 + 2KOH = 2KBr + 2H_2O + C_{10}H_{14}.$$

By oxidation with warm nitric acid terebenthene is converted into terebic acid (§ 867), and, on passing its vapours over soda lime heated to 400°, into *terebentilic acid*, $C_8H_{10}O_2 = C_6H_6\left\{\begin{matrix}CH_3\\CO.OH\end{matrix}\right.$ (?); this latter crystallises in small white needles, melts at 90°, and boils at 250°.

1120. *Compounds with One Molecule of Hydrochloric Acid.*—The turpentine oils absorb large quantities of hydrochloric acid gas, forming with it two isomeric compounds of the formula $C_{10}H_{17}Cl$. If the temperature is kept as low as possible, a crystalline body is chiefly formed; at higher temperatures a liquid addition product is mainly obtained. They are separated by solution in hot alcohol. On cooling the first separates in colourless needles of camphoraceous odour (artificial camphor). It is insoluble in water, melts at 115° (or in an atmosphere of hydrochloric acid gas, with special precautions to prevent decomposition, at 131°–132°), and can be sublimed on careful heating.

1121. *Camphenes.*—Both the isomeric hydrochlorides, on heating with basic hydrates or alkali salts of weak acids, are re-converted into hydrocarbons of the original formula, but which show altered properties. The crystalline hydrochlorides, on heating with dry soap at 220°, give solid *camphenes*, melting at 45° and boiling at 160° (terecamphene being lævorotary and austracamphene dextrorotary). By decomposition with sodic benzoate both hydrochlorides yield optically inactive *camphene*, which also melts at 45° and boils at 160°. All three camphenes unite directly with a molecule of hydrochloric acid, forming solid hydrochlorides. By decomposition with lime heated to 200° these yield a liquid inactive terpene, *camphilene*, boiling at 160°, which also yields a solid compound, $C_{10}H_{17}Cl$, with hydrochloric acid.

The original liquid hydrochlorides. on the other hand, are converted by heated lime into a liquid, *terebilene*, which is optically inactive, and forms a liquid hydrochloride, $C_{10}H_{17}Cl$.

Terebene (§ 1119) yields a solid hydrochloride, which melts in an atmosphere of hydrochloric acid at 125° and, unlike its isomers, is quickly decomposed by water into hydrochloric acid and solid *camphene.*

1122. *Compounds with Two Molecules of Hydrochloric Acid.*—On long contact of turpentine oils with concentrated hydrochloric acid, or by saturation of their solutions in alcohol, ether, and acetic acid with hydrochloric acid gas, rhombic crystals are formed of the dihydrochlorides, $C_{10}H_{18}Cl_2$; they are insoluble in water, but on long boiling with it yield terpinol, $C_{20}H_{34}O$.

1123. *Terpine.*—Colourless crystals of *terpine hydrate* separate after a time from oil of turpentine containing water:

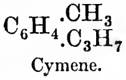
$$C_{10}H_{22}O_3 = C_{10}H_{20}O_2,H_2O.$$

These are obtained in quantity when eight parts of oil of turpentine, two parts of dilute nitric acid, and one part of alcohol are allowed to react on one another for some time, the mixture being frequently shaken. Terpine hydrate forms large, brilliant, colourless, short rhombic prisms, and can be crystallised from alcohol, ether, and hot water. In an exsiccator it loses a molecule of water and is converted into *terpine*, $C_{10}H_{20}O_2$, which melts at 103° and sublimes at higher temperatures in long needles. Hydrochloric acid and phosphoric chloride convert it into the above-mentioned dihydrochloride:

$$C_{10}H_{18}Cl_2.$$

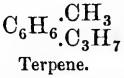
On long heating of its aqueous solution with some hydrochloric and sulphuric acids it yields *terpinol*, $C_{20}H_{34}O$. This latter is a liquid of hyacinth-like odour; it boils at 168° and has sp. gr. ·852. Hydrochloric acid reconverts it into $C_{10}H_{18}Cl_2$.

The relations of these bodies to one another are shown in the following formula:



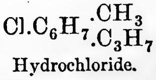
$$C_6H_4\begin{matrix}.CH_3\\.C_3H_7\end{matrix}$$

Cymene.



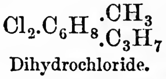
$$C_6H_6\begin{matrix}.CH_3\\.C_3H_7\end{matrix}$$

Terpene.



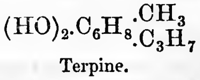
$$Cl.C_6H_7\begin{matrix}.CH_3\\.C_3H_7\end{matrix}$$

Hydrochloride.



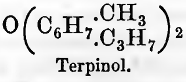
$$Cl_2.C_6H_8\begin{matrix}.CH_3\\.C_3H_7\end{matrix}$$

Dihydrochloride.



$$(HO)_2.C_6H_8\begin{matrix}.CH_3\\.C_3H_7\end{matrix}$$

Terpine.



$$O\left(C_6H_7\begin{matrix}.CH_3\\.C_3H_7\end{matrix}\right)_2$$

Terpinol.

Other Terpenes.

1124. *Citrene* is the ethereal oil obtained from lemon peel. It boils at 173° and has sp. gr. ·85 at 15°. Hydrochloric acid readily converts it into *citrene dihydrochloride*, $C_{10}H_{18}Cl_2$, melting at 44°;

water converts it into the crystalline *citrene terpine*, $C_{10}H_{20}O_2$; and with bromine it yields a dibromide, $C_{10}H_{16}Br_2$, which with aniline at 190° gives aniline hydrobromide and cymene. The ethereal oils from other aurantiaceæ, such as oil of bergamot, &c., are very similar to oil of lemons.

The greater number of *ethereal oils*, which are obtained by distillation of odoriferous plants with water, are mixtures of terpenes with other volatile substances. When these admixtures are solid they crystallise out in the cold and are termed *stearoptenes*. A large number of these oils have been previously mentioned; e.g. oil of rue (§ 455), Roman chamomile oil (§ 797, 2), oil of anise (§ 1100), winter green oil (§ 1061, 1), oil of spireæ (§ 1033), oil of thyme (§ 1023), oil of cinnamon (§ 1092), oil of cloves (§ 1101), &c.

CAMPHORS.

1125. The camphors stand in very close relation to cymene and to the terpenes; they are obtained, mostly with terpenes, by distillation of different plants with water.

The most important varieties, *borneol*, $C_{10}H_{18}O$, and *laurinol*, $C_{10}H_{16}O$, stand to one another in the relation of a secondary alcohol to its ketone. Menthol, $C_{10}H_{20}O$, is a similar alcohol-like substance.

1126. *Borneol*, or *Borneo camphor*, $C_{10}H_{17}.OH$, occurs together with borneene, a terpene, in *Dryobalanops Camphora*, growing in Borneo and Sumatra. It can be obtained from ordinary camphor by heating with alcoholic potassic hydrate:

$$2C_{10}H_{16}O + KOH + HO.C_2H_5 = 9C_{10}H_{18}O + KO.C_2H_3O,$$

together with campholic acid (§ 1129), similarly, together with camphor-carbonic acid, by treatment of laurinol with sodium and carbonic anhydride.

Borneol forms brittle crystals, possessing at once a camphor- and peppermint-like odour; it melts at 198° and boils at 212°. The alcoholic solution rotates the plane of polarisation to the right ($[\alpha]_D = +32{\cdot}7°$). On oxidation with nitric acid it yields laurinol, or on further action camphoric acid; by heating with phosphoric anhydride it is resolved into water and *borneene*, boiling at 176°–180°:

$$C_{10}H_{18}O + P_2O_5 = 2HPO_3 + C_{10}H_{16}.$$

On heating with organic acids at 200° borneol yields salts. *Borneol stearate*, $C_{10}H_{17}.O.C_{18}H_{35}O$, is a viscous oil which slowly crystallises. Concentrated hydrochloric acid, and still more readily phosphoric chloride, convert borneol into *borneyl chloride*, $C_{10}H_{17}Cl$, which resembles the isomeric terebenthene hydrochloride very closely, but melts at 159° and decomposes at a little higher temperature.

An optically *lævorotary borneol* occurs in the fusel oil from the spirit prepared from the fermentation of madder roots; other isomeric compounds exist in oil of hops, oil of cajeput, oil of coriander seed, &c.

A compound homologous to borneol is contained in oil of patchouli; this *patchouli camphor*, $C_{15}H_{28}O$, is crystalline, melts at 54°–55°, and boils at 296°.

1127. *Laurinol*, more commonly termed *camphor*, is obtained from all parts (especially from the wood) of *Laurus Camphora*; it is purified by sublimation. It can be prepared by the oxidation of oil of valerian and oil of sage or borneol with nitric acid.

Camphor occurs in commerce in transparent tough masses of peculiar smell and taste. It forms large brilliant crystals on slow sublimation (even at ordinary temperatures) and on evaporation of its alcoholic solution. Its sp. gr. is ·985, the vapour density 5·32; it melts at 175° and boils at 205°. It is very little soluble in water, readily soluble in alcohol, ether, and oils. Its alcoholic solution is strongly dextrorotary.

Aqueous hypochlorous acid converts camphor into *monochlorcamphor*, $C_{10}H_{15}ClO$, a crystalline mass, melting at 95°, readily soluble in alcohol and ether; on heating with alcoholic potassic hydrate this yields *oxycamphor*, $C_{10}H_{16}O_2 = C_{10}H_{15}(OH)O$, forming colourless needles. It melts at 137° and can be sublimed.

A saturated solution of camphor in chloroform, on treatment with bromine, yields a crystalline *camphor dibromide*, $C_{10}H_{16}OBr_2$, which readily decomposes into hydrobromic acid and *monobrom-camphor*. This latter forms colourless prisms, melts at 76°, and boils at 274°; it is also formed, together with *dibrom-camphor*, $C_{10}H_{14}Br_2O$ (prisms melting at 114·5°), by heating camphor and bromine at 120°.

Sodium dissolves readily in a solution of camphor in toluene, much heat being evolved and sod-camphor and borneol being formed:

$$3C_{10}H_{16}O + Na_2 = 2C_{10}H_{15}NaO + C_{10}H_{18}O.$$

Sod-camphor unites directly with carbonic anhydride, forming *sodic campho-carbonate*:

$$C_{10}H_{15}ONa + CO_2 = C_{10}H_{15}O.CO.ONa,$$

from whose aqueous solution hydrochloric acid separates *campho-carbonic acid* in small difficultly soluble crystals; it melts at 118°–119°, with decomposition into carbonic anhydride and camphor.

1128. *Matricaria camphor* is obtained from the oil of feverfew (*Matricaria Parthenium*) by strongly cooling that portion which distils between 200° and 220°. It is isomeric with laurinol, and resembles it in all but its optical properties, this body being lævorotary. This difference in rotary power runs through all the derivatives of these bodies, though in all other respects they are closely analogous.

Both camphors are acted on by phosphoric chloride, being first converted into crystalline dichloride, $C_{10}H_{16}Cl_2$, but partly further, with elimination of hydrochloric acid, into solid, $C_{10}H_{15}Cl$ (comp. § 445). This latter on heating again loses hydrochloric acid and is converted into cymene.

On distillation with zincic chloride, phosphoric anhydride, or phosphoric sulphide, camphor yields cymene in addition to xylene and toluene; thiocymophenol also in the last case, whilst heating with $\frac{1}{5}$ of its weight of iodine, converts it into cymophenol (§ 1023).

Two isomers of camphor exist in the oil of wormwood, obtained from *Artemisia Absinthium* when in flower, *absinthol*, boiling at 195°, and *myristicol*, boiling at 212°–218°; they both yield cymene on distillation with zincic chloride or phosphoric sulphide.

Acids from Camphor.

1129. By the action of strong basic hydrates on camphor, whether effected by passing camphor vapour over heated soda lime or by boiling for a long time with alcoholic potassic hydrate, borneol and campholates are formed :

$$C_{10}H_{16}O + HOK = C_{10}H_{17}O.OK,$$

from whose aqueous solution addition of acids separates *campholic acid*, $C_{10}H_{18}O_2$. It is nearly insoluble in water, crystallises from alcohol in colourless prisms or plates, melts at 95°, and can be sublimed. On distillation of its calcic salt with soda lime, or on heating the acid with phosphoric anhydride, it is converted into *campholene*, C_9H_{16}, an oil boiling at 135°.

Nitric acid dissolves camphor in the cold without alteration, but on heating vigorous oxidation ensues, which is only completed after boiling for several days (150 grams camphor being heated with two litres of nitric acid of sp. gr. 1·37). On evaporating the liquid much camphoric acid separates in the crystalline form, and a syrupy mother liquor is left, from which camphoronic acid, a product of the further oxidation of camphoronic acid, can be obtained.

1130. *Camphoric acid*, $C_{10}H_{16}O_4 = C_8H_{14}(CO.OH)_2$, probably a homologue of fumaric and the pyrocitric acids (§§ 896–7), crystallises from a hot saturated aqueous solution in shining colourless plates, melts at 178°, and decomposes at slightly higher temperature into water and *camphoric anhydride*, $C_{10}H_{14}O_3 = C_8H_{14}(CO)_2O$; this latter sublimes in long shining prisms and melts at 217°.

Camphoric acid is dibasic, and yields acid and normal salts. Calcic camphorate, $C_{10}H_{14}CaO_4,8H_2O$, is readily soluble in water and decomposes at higher temperatures into calcic carbonate and phorone (§ 444) :

$$C_{10}H_{14}CaO_4 = CaCO_3 + C_9H_{14}O.$$

When prepared from ordinary camphor, camphoric acid in alcoholic solution rotates the plane of polarisation of light to the right ($[\alpha] = +38°–39°$); that prepared from matricaria camphor is lævorotary to exactly the same extent, though otherwise of similar properties. These two modifications behave to one another like tartaric and antitartaric acid, combining in equal molecules to form an inactive camphoric acid corresponding to racemic acid (comp. § 907). Long heating at 150° with concentrated hydrochloric acid converts dextrorotary camphoric acid into a second inactive modification, *mesocamphoric acid*. This crystallises in interlaced needles, melts at 113°, and is soluble in water.

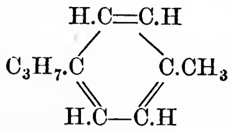
1131. *Camphoronic acid*, $C_9H_{12}O_5$, is formed by the further action of nitric acid on camphoric acid, and occurs in the syrupy mother liquor from which this has been crystallised; this mother liquor is neutralised with ammonia, heated to boiling, and baric chloride added, when baric camphornate, $(C_9H_9O_5)_2Ba_3,2H_2O$, is precipitated, which yields camphoronic acid when decomposed by dilute sulphuric acid. Camphoronic acid, $C_9H_{12}O_5,H_2O$, crystallises in small needles, loses its water of crystallisation at 110°, and melts at 115°; it sublimes unchanged at higher temperatures; on fusion with alkalies it yields butyric acid. It is a tribasic acid.

1132. *Menthol*, the stearoptene of peppermint oils, is usually considered as belonging to the camphors. It contains two atoms of hydrogen more than borneol, having the formula:

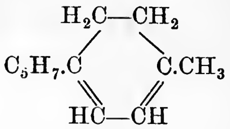
$$C_{10}H_{20}O = C_{10}H_{19}OH.$$

It crystallises in prisms, has a peppermint-like odour, melts at 42°, and boils at 212°. It behaves like a monhydric alcohol, forming salts with acids. When treated with hydrochloric acid or phosphoric chloride it yields *menthyl chloride*, $C_{10}H_{19}Cl$, and with phosphoric anhydride it gives *menthene*, $C_{10}H_{18}$, an oil boiling at 163°.

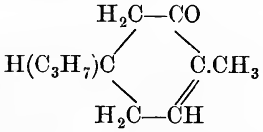
The constitution of the terpenes and camphors is still far from settled. The following formulæ have been suggested, but, especially in the case of the camphors and their derivatives, must be accepted with great reserve:



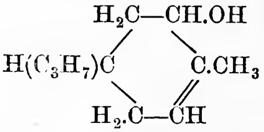
Cymene.



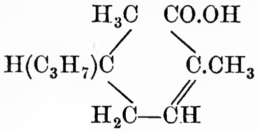
Terpene.



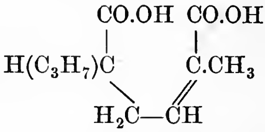
Laurinol.



Borneol.



Campholic acid.



Camphoric acid.

Indigo Group.

1133. Many species of plants, especially the subtropical and tropical *indigoferæ*, *Isatis tinctoria*, *Polygonum tinctorium*, &c., and at times also the urine of man and mammalia, contain a substance (probably of glucoside nature) which by ferment-like decompositions, or by boiling with dilute acids, yields *indigo blue*.

This chromogen has been prepared from *Isatis tinctoria* (woad) and termed *indican*. For this purpose the dried plant is extracted with alcohol, the filtered liquid evaporated at ordinary temperatures, the residue dissolved in water and shaken with cupric hydrate; it is then filtered, the filtrate treated with sulphuretted hydrogen to remove copper, and the clear solution evaporated over sulphuric acid.

Indican is a clear brown syrup of bitter and nauseous taste; it is decomposed by boiling with dilute sulphuric acid into *indiglucin*:

$$C_6H_{10}O_6 \ (?),$$

and indigo blue, which precipitates. Indiglucin is also a syrup of faintly sweet taste; it reduces Fehling's solution (§ 870), but will not enter into alcoholic fermentation with yeast.

In order to prepare indigo on the large scale, the leaves and stems of the respective plants are covered with water and allowed to ferment. The liquid is then poured into shallow vessels and exposed to the air, when, in consequence of the oxidation of the indigo white first formed, it deposits the blue colouring matter. This latter is washed and dried, and then constitutes commercial indigo.

This is by no means pure indigo blue; it yields *indigo gluten* to dilute acetic acid, *indigo brown* to potassic hydrate solution, and finally *indigo red* to boiling alcohol. The residue then consists of indigo blue mixed with insoluble impurities.

1134. *Indigo blue*, or *indigotine*, $C_{16}H_{10}N_2O_2$, is obtained synthetically by heating a mixture of isatine with phosphorous trichloride, phosphorus, and chlor-acetyl in sealed tubes at 70°–80° for several hours; when the reaction product is poured into water, on exposure to air, blue flocks separate. It is also obtained by the reduction of isatine chloride, and very readily by treatment of potassic indoxyl sulphonate with ferric chloride and sulphuric acid.

A still more important method of synthesis is effected as follows: Cinnamic acid is converted into orthonitro-cinnamic acid; this is then brominated and treated with potassic hydrate, whereby it is converted into nitro-phenyl propiolic acid (comp. § 1101), which latter on reduction (best by glucose in alkaline solution) yields indigo blue:

$$2C_9H_5(NO_2)O_2 + 2H_2 = C_{16}H_{10}N_2O_2 + 2H_2O + 2CO_2.$$

The commercial indigo blue can be purified by reducing it to indigo white, which yields metallic compounds with the alkalies or alkaline earths which are soluble in water. The reducing agents generally employed are ferrous salts, grape sugar, or putrefying organic matter; e.g. 3 parts indigo with 6 parts quick lime, 400–500 parts water, and 4 parts ferrous sulphate, or equal parts of indigo and grape sugar with $1\frac{1}{2}$ part concentrated sodic hydrate solution. The resulting yellow solution of the indigo-white metallic compound, on exposure to air, deposits indigo blue in small crystals.

Pure indigotine can also be obtained in well-formed crystals by treating commercial indigo with boiling aniline and slowly cooling the filtered liquid.

Indigotine is a deep blue substance with metallic copper-red reflex from the crystal faces. It is quite insoluble in water, alcohol, ether, mineral acids, and alkalies. At about 300° it forms a beautiful purple red vapour, which condenses again to copper-coloured prisms of pure indigotine.

On boiling indigo blue with solution of potassic hydrate and manganic oxide it is converted into orthamido-benzoic acid (§ 1056), whilst by dry distillation with solid potassic hydrate it yields aniline.

1135. The reduction to indigo white in presence of strong bases has been already mentioned. From the alkaline liquid *indigo white*, $C_{16}H_{12}N_2O_2$, can be separated by over-saturating with hydrochloric acid; air being excluded, the precipitated white flocks, which slowly unite to crystalline scales, being washed with air-free water and dried in vacuo. It is obtained in this way as a shimmering powder, dissolving in alcohol, ether, alkalies, and lime, or baryta water, with yellow colour. When moist it oxidises with great rapidity to indigo blue:

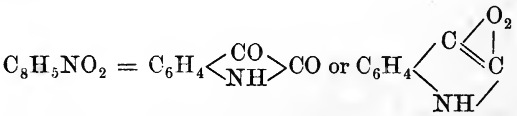
$$C_{16}H_{12}N_2O_2 + O = H_2O + C_{16}H_{10}N_2O_2.$$

1136. By digestion of indigotin with concentrated sulphuric acid, or with weak Nordhausen sulphuric acid, two *indigotin sulphonic acids* are formed—*indigotin monosulphonic acid,* or *phœnicin sulphuric acid,* $C_{16}H_9(SO_2.OH)N_2O_2$, and *indigotin disulphonic acid,* or *sulphindigotic acid,* $C_{16}H_8(SO_2.OH)_2N_2O_2$. The latter alone is formed when 1 part of indigo is heated with 15 parts of sulphuric acid for three days at 40°–50°, whilst a mixture of both is obtained if only 8 parts of sulphuric acid be employed.

Phœnicin sulphuric acid, being insoluble in dilute acids, separates as a blue powder on dilution of the reaction product with water. It is soluble in alcohol and pure water, and yields monobasic salts with metals; e.g. $C_{16}H_9(SO_2.OK)N_2O_2$, which is precipitated in purple flocks on addition of potassic acetate to a concentrated solution of phœnicin sulphuric acid.

Sulphindigotic acid is completely removed from the diluted solution of indigo in sulphuric acid by the introduction of wool. The deep blue coloured wool is then treated with dilute ammonia, when ammonic sulphindigotate goes into solution, and on addition of plumbic acetate yields a dark blue precipitate of the lead salt. This is suspended in water and decomposed with sulphuretted hydrogen. By this, however, the sulphindigotic acid is reduced to *indigo-white disulphonic acid,* $C_{16}H_{10}(SO_2.OH)_2N_2O_2$, sulphur being precipitated. The colourless filtrate rapidly oxidises on exposure to air, again yielding sulphindigotic acid, which on evaporation is obtained as an amorphous blue mass, readily soluble in water and alcohol. The salts of sulphindigotic acid are difficultly soluble in water. The *potassic salt,* $C_{16}H_8(SO_2.OK)_2N_2O_2$, is the most important, as it is obtained from the crude sulphindigotic acid by precipitation with potassic carbonate or acetate, and brought into commerce as a blue colouring material under the name of *indigo carmine.*

1137. *Isatine:*

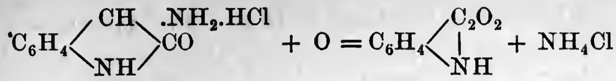


$$C_8H_5NO_2 = C_6H_4\left\langle\begin{matrix}CO\\NH\end{matrix}\right\rangle CO$$

Indigo is suspended in three times its weight of boiling water, and nitric acid of sp. gr. 1·35 slowly added until the blue colour has disappeared; on cooling the solution deposits *isatine,* which is purified by solution in potash, precipitation with hydrochloric acid, and crystallisation from alcohol, when it forms brilliant yellowish red prisms. It is readily dissolved by ether and boiling water, and still more so by boiling alcohol. Potassic hydrate dissolves it, forming a violet solution of potassium isatine, which, on addition of argentic nitrate, gives difficultly soluble carmine red crystals of *silver isatine:*

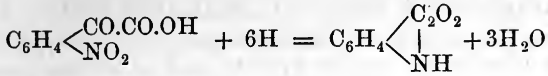
$$C_8H_4NO_2Ag.$$

Isatine has been obtained synthetically by the action of oxidising agents on amido-oxindol:



$$C_6H_4\Big\langle\begin{array}{l}CH.NH_2.HCl\\ NH\end{array}\Big\rangle CO + O = C_6H_4\Big\langle\begin{array}{l}C_2O_2\\ \;|\\ NH\end{array} + NH_4Cl$$

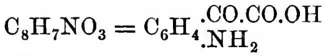
and by the reduction of orthonitro-phenyl glyoxalic acid in alkaline solution:



$$C_6H_4\Big\langle\begin{array}{l}CO.CO.OH\\ NO_2\end{array} + 6H = C_6H_4\Big\langle\begin{array}{l}C_2O_2\\ \;|\\ NH\end{array} + 3H_2O$$

On strongly heating isatine fuses and sublimes in part unchanged. It yields crystalline compounds with alkaline hydric sulphites; e.g. on saturating a solution of potassium isatine with sulphurous anhydride, yellow plates separate, of the formula $C_8H_5NO_2,KHSO_3$. which yield isatine on treatment with hydrochloric acid. On distilling isatine with concentrated solution of potassic hydrate aniline passes over; on addition of nitrous acid, nitrogen is evolved and nitro-salicylic acids formed. Boiling with strong nitric acid also first converts it into nitro-salicylic acid and finally into trinitro-phenol. By ammonia it is (especially in alcoholic solution) converted into different amide derivatives, water being eliminated.

On boiling the violet solution of potassium isatine its colour changes to yellow, and then contains *potassic isatate*, $C_8H_6NKO_3$, which, on addition of plumbic acetate, gives a precipitate of plumbic isatate. On suspending this in water and decomposing with sulphuretted hydrogen, and then evaporating the filtrate in vacuo, a white flocculent precipitate is obtained of *isatic acid* or *trioxindol:*



$$C_8H_7NO_3 = C_6H_4\begin{array}{l}.CO.CO.OH\\ .NH_2\end{array}$$

which easily decomposes on heating into isatine and water.

A hot boiling isatine solution yields, on treatment with chlorine, a yellow flocculent precipitate of *chlor-isatine*, $C_8H_4ClNO_2$. Indigo, when suspended in water and treated with chlorine, yields a mixture of products from which boiling water extracts chlor-isatine, together with *dichlor-isatine*, $C_8H_3Cl_2O_2N$. They can be separated by alcohol, in which the latter is more readily soluble. Dichlor-isatine crystallises in orange yellow four-sided prisms of bitter taste.

Sulphindigotic acid on oxidation yields *isatine sulphonic acid:*

$$C_8H_4(SO_2.OH)NO_2,$$

readily soluble in water.

1138. *Reduction Products of Isatine.*—Isatine combines with nascent hydrogen, evolved from zinc and hydrochloric acid, forming *isatyde*, $C_{16}H_{12}N_2O_4$, which separates as a white crystalline powder, difficultly soluble in alcohol and ether, insoluble in water. Isatine suffers the same change (which resembles the formation of indigo white from indigo) on long contact with ammonic sulphide.

On passing sulphuretted hydrogen into an alcoholic solution of isatine, sulphur and isatyde are precipitated, whilst *sulphisatyde:*

$$C_{16}H_{12}N_2O_2S_2,$$

remains dissolved and is precipitated by addition of water as a greyish yellow powder:

$$2C_8H_5NO_2 + 3H_2S = S + 2H_2O + C_{16}H_{12}N_2O_2S_2.$$

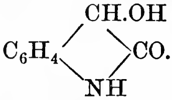
On rubbing together sulphisatyde with alcoholic potassic hydrate, and washing the rose-coloured mass with water, a residue is obtained of *indine*, $C_{16}H_{10}N_2O_2$, isomeric with indigotine:

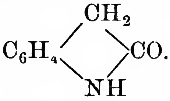
$$C_{16}H_{12}N_2O_2S_2 + 2KOH = C_{16}H_{10}N_2O_2 + 2H_2O + K_2S_2.$$

It forms a fine red powder, which dissolves on heating with excess of alcoholic solution of potassic hydrate, and on cooling gives black crystals of *potassium indine*, $C_{16}H_9KN_2O_2$.

1139. Another series of reduction products are formed by the action of sodium amalgam on aqueous solutions of alkaline isatates. On evaporating the liquid brilliant crystals of *sodium dioxindol* separate:

$$C_8H_6NaNO_3 + 2H = H_2O + C_8H_6NaNO_2,$$

from which hydrochloric acid liberates *dioxindol*, also termed *hydrindic acid*, $C_8H_7NO_2 =$  $C_6H_4\left\langle\begin{matrix}CH.OH\\NH\end{matrix}\right\rangle CO$. Dioxindol dissolves readily in water and alcohol, crystallises in transparent yellow prisms, and yields saline compounds with both bases and acids; e.g. $C_8H_7NO_2,HCl$. On exposure to air it oxidises readily into isatine, and on treatment of its alcohol solution with nitrous anhydride it yields *nitroso-dioxindol*, $C_8H_6(NO)NO_2$, a crystalline substance, melting at above 300°. Gentle heating with nitric acid converts dioxindol into benzoic aldehyde.

In dilute acid solution dioxindol is converted by nascent hydrogen into *oxindol*, $C_8H_7NO_2$. This body is also obtained by the reduction of orthonitro-phenyl acetic acid, and therefore appears to be an inner-anhydride of orthamido-phenyl acetic acid, its structural formula being  $C_6H_4\left\langle\begin{matrix}CH_2\\NH\end{matrix}\right\rangle CO$. It crystallises in colourless needles, melts at 120°, and can be distilled unaltered in small quantity; it dissolves readily in hot water and alcohol. Exposed to air, its aqueous solution oxidises again to dioxindol. It yields saline compounds with metals and bases; with nitrous acid it gives *nitroso-oxindol:*

$$C_8H_6(NO)NO,$$

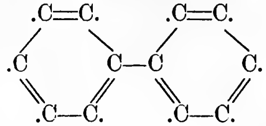
crystallising in golden yellow needles, difficulty soluble in water.

Indol, C_8H_7N, is obtained by passing the vapours of oxindol over heated zinc, or by distilling a mixture of zinc and the brownish yellow powder obtained by long boiling of indigo blue with zinc and hydrochloric acid. It is prepared synthetically from nitro-cinnamic acid by heating with potassic hydrate and zinc filings. It forms large colourless prisms, which melt at 52°, and yields by combination with hydrochloric acid a difficultly soluble salt, decomposed into its constituents on boiling with water.

1140. The constitution of indol and indigo is still undetermined; their method of formation leaves no doubt that the benzene nucleus has the nitrogen atom and the dicarbon nucleus united to it in the ortho position, but with regard to the distribution of the hydrogen and oxygen atom (in the case of indigo) nothing is yet known with certainty.

COMPOUNDS OF CONJUGATED BENZENE NUCLEI.

1141. Several benzene nuclei can unite to form fresh groups, the union being either direct, e.g.

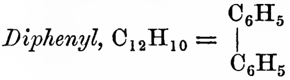


or by means of other carbon atoms, e.g.

$$.\underset{\cdot}{\ddot{C}}_{\underset{\cdot}{6}}-\underset{\cdot}{\dot{C}}-\underset{\cdot}{\ddot{C}}_{\underset{\cdot}{6}}.$$

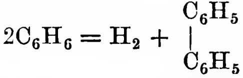
These groups may be designated as *conjugated benzene nuclei.* The hydrocarbons derived from them are capable of the same substitutions as benzene itself, so that, on account of the complication of the carbon nucleus, an extraordinary number of isomeric compounds appears to be possible, although, from the short time these bodies have been worked at, only a moderate number are known at present.

Compounds Containing Two Benzene Groups.



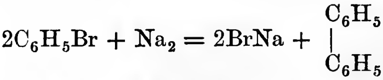
$$\textit{Diphenyl}, C_{12}H_{10} = \begin{array}{c}C_6H_5\\ |\\ C_6H_5\end{array}$$

1142. When the vapour of benzene is sent through tubes filled with pumice and heated to redness, diphenyl is formed along with free hydrogen and other products:



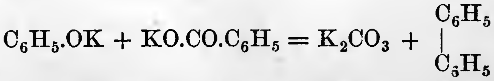
$$2C_6H_6 = H_2 + \begin{array}{c}C_6H_5\\ |\\ C_6H_5\end{array}$$

The same hydrocarbon is also formed by acting on an ethereal solution of brom-benzene with sodium:



$$2C_6H_5Br + Na_2 = 2BrNa + \begin{array}{c}C_6H_5\\ |\\ C_6H_5\end{array}$$

also by the dry distillation of a mixture of potassic phenylate and potassic benzoate or oxalate:



$$C_6H_5.OK + KO.CO.C_6H_5 = K_2CO_3 + \begin{array}{c}C_6H_5\\ |\\ C_6H_5\end{array}$$

$$2C_6H_5.OK + K_2C_2O_4 = 2K_2CO_3 + C_{12}H_{10}$$

and is also found in small quantity in coal-tar oils.

Diphenyl crystallises in large brilliant white or colourless leafy crystals, of an agreeable odour, easily soluble in alcohol and ether, but quite insoluble in water.

It melts at 70·5° and boils at 254°. Chromic acid oxidises it in glacial acetic solution to benzoic acid, one phenyl group being destroyed.

Parachlor-diphenyl, $C_6H_4Cl.C_6H_5$, prepared from phenyl-phenol (§ 1144) by means of PCl_5, crystallises in plates, melting at 75° and yielding parachlor-benzoic acid on oxidation.

Brom-diphenyls.—Parabrom-diphenyl, $C_6H_4Br.C_6H_5$, obtained by treating one molecule of diphenyl in solution in carbonic disulphide with a molecule of bromine, forms colourless crystals, melting at 89° and boiling at 310°; it gives parabrom-benzoic acid on oxidation.

Diphenyl treated under water with excess of bromine yields *dibrom-diphenyl*, $C_6H_4Br.C_6H_4Br$; it forms large colourless prisms, almost insoluble in alcohol, melting at 64° and boiling between 355°–360°.

1143. *Nitro-diphenyls.*—1. *Paranitro-diphenyl*, $C_6H_4(NO_2).C_6H_5$, resulting from the direct action of cold concentrated nitric acid on the hydrocarbon, crystallises in colourless needles, melting at 113° and boiling at 340°, and giving paranitro-benzoic acid on oxidation with chromic acid.

2. The isomeric *metanitro-diphenyl* is obtained by distilling a mixture of sand, metanitro-benzoic acid, and potassium phenylate; it forms large prisms, melting at 86° and much more readily soluble in alcohol than the para compound, $C_{12}H_8(NO_2)_2$.

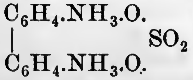
Two isomeric dinitro-diphenyls result from the action of excess of cold fuming nitric acid on diphenyl. The *para compound* is only slightly soluble in alcohol, and crystallises in colourless needles, melting at 233°, which by oxidation yield paranitro-benzoic acid.

The *isodinitro-diphenyl* is easily soluble in alcohol, and melts at 93·5°.

Amido-diphenyls. — Paranitro-diphenyl is reduced by tin and hydrochloric acid to *para-amido-diphenyl*, $C_6H_4(NH_2).C_6H_5$, crystallising in colourless needles, melting between 49°–50°; and the two dinitro-diphenyls give by incomplete reduction the isomeric compounds $C_{12}H_8(NO_2).(NH_2)$, *para-amido-nitro-diphenyl*, melting at 198°, and *isamido-nitro-diphenyl*, at 97°–98°. Both compounds crystallise in red needles.

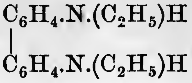
Paradiamido-diphenyl, $C_6H_4.(NH_2).C_6H_4(NH_2)$, or *benzidine*, is formed by the reduction of paradinitro-diphenyl with tin and hydrochloric acid, as well as by the action of acids on the isomeric hydrazobenzene (§ 975), also by heating azobenzene with concentrated hydrochloric acid to 115° and by the decomposition of brom-aniline with sodium (§ 986).

It crystallises in silvery plates, melting at 118°, which may be partly sublimed unchanged; it is soluble in hot water, more readily in alcohol and ether, and forms difficultly soluble salts, e.g.



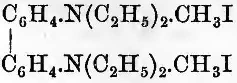
$$\begin{array}{l} C_6H_4.NH_3.O. \\ | \qquad\qquad\quad SO_2 \\ C_6H_4.NH_3.O. \end{array}$$

almost insoluble in water and alcohol. It combines with ethylic iodide to form diphenyl-diethyl diammonic iodide, from which alkalies liberate *diethyl benzidine :*



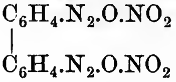
$$\begin{array}{l} C_6H_4.N.(C_2H_5)H \\ | \\ C_6H_4.N.(C_2H_5)H \end{array}$$

which again, by a repetition of the treatment, yields *tetraethyl benzidine,* and this further combines with methylic iodide, forming *tetraethyl-dimethyl benzidine diiodide :*



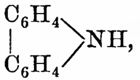
$$\begin{array}{l} C_6H_4.N(C_2H_5)_2.CH_3I \\ | \\ C_6H_4.N(C_2H_5)_2.CH_3I \end{array}$$

An aqueous solution of benzidine is converted by nitrous acid into *tetra-azodiphenyl nitrate :*



$$\begin{array}{l} C_6H_4.N_2.O.NO_2 \\ | \\ C_6H_4.N_2.O.NO_2 \end{array}$$

which, by addition of ether alcohol, is precipitated in yellowish explosive needles.

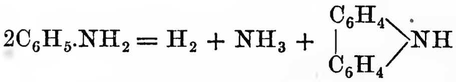
Carbazol, or *imido-diphenyl,*  is obtained from that portion of coal tar boiling between 320°–360° by addition of picric acid to the solution of this fraction in toluol, when the salt

$$C_{12}H_8.NH_2.O.C_6H_2(NO_2)_3$$

separates in large red needles, melting at 182°.

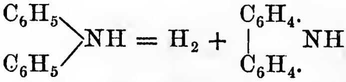
Ammonia liberates from this salt free carbazol, which crystallises from hot alcohol or benzene in colourless plates, melting at 238° and boiling between 354° and 355°. It scarcely possesses basic properties, but dissolves in sulphuric acid with production of yellowish solutions. By heating with hydriodic acid and phosphorus at 240° it is converted into *carbazoline,* $C_{12}H_{15}N$, a basic body crystallising in prisms, melting at 99°, and boiling at 297°.

Another method for the production of carbazol consists in passing the vapour of aniline or diphenylamine through ignited tubes :



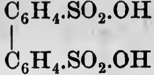
$$2C_6H_5.NH_2 = H_2 + NH_3 + \begin{array}{l} C_6H_4 \\ | \\ C_6H_4 \end{array} \!\!> NH$$

and



$$\begin{array}{l} C_6H_5 \\ C_6H_5 \end{array} \!\!> NH = H_2 + \begin{array}{l} C_6H_4. \\ | \\ C_6H_4. \end{array} NH$$

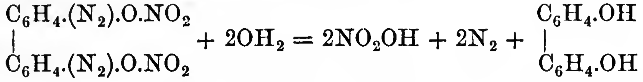
An isomer of carbazol, *acridine,* is also found in the 320°–360° fraction of coal tar, from which it may be extracted by dilute sulphuric acid. It crystallises in colourless rhombic crystals, melting at 107°, subliming at 100°, and boiling above 360°. It is easily soluble in alcohol and ether, and is specially characterised by the insolubility of its chromate. When brought in contact with the skin it causes great irritation and burning pain.

1144. *Diphenyl sulphonic acids* result by heating diphenyl with concentrated sulphuric acid. By excess of acid *diphenylene disulphonic acid*,  $\begin{array}{l} C_6H_4.SO_2.OH \\ | \\ C_6H_4.SO_2.OH \end{array}$, is alone produced; by excess of diphenyl, however, a mixture of the latter with *paraphenyl phenylene sulphonic acid*, $C_6H_5.C_6H_4.SO_2.OH$. Since the copper salt of the monosulphonic acid is difficultly soluble even in boiling water, whilst that of the disulphonic acid is readily soluble, they may be separated without any difficulty. The disulphonic acid crystallises in prisms, melting at 72·5° and readily soluble in water.

Phenyl Phenols and Oxides.—The corresponding phenols are produced by melting the potassium salts of the diphenyl sulphonic acids with potash and decomposition of the products with dilute sulphuric acid.

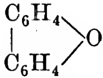
Phenyl-phenol, $C_{12}H_{10}O = C_6H_5.C_6H_4.OH$, or *diphenylol*, prepared from phenyl phenylene sulphonic acid, forms colourless microscopic needles, melting at 164°–165°, very volatile in steam, and boiling at 305° or 308°.

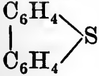
Diphenol, $C_{12}H_{10}O_2 = HO.C_6H_4.C_6H_4.OH$, in addition to its production from diphenylene disulphonic acid, is also obtainable by boiling tetrazodiphenyl nitrate with water:



$$\begin{array}{l} C_6H_4.(N_2).O.NO_2 \\ | \\ C_6H_4.(N_2).O.NO_2 \end{array} + 2OH_2 = 2NO_2OH + 2N_2 + \begin{array}{l} C_6H_4.OH \\ | \\ C_6H_4.OH \end{array}$$

It crystallises in colourless plates, which do not decompose on sublimation.

Diphenylene oxide, $C_{12}H_8O$ =  $\begin{array}{l} C_6H_4 \\ | \\ C_6H_4 \end{array}\!\!>O$, results when phenol is heated with plumbic oxide, or phenyl phosphoric ether with excess of lime (§ 961). It is insoluble in water, soluble in alcohol, ether, and benzene, from which it crystallises in plates of 80°–81° melting point, boils at 287°, and possesses an agreeable odour.

Phenyl sulphide (§ 962) is decomposed when its vapour is passed through red-hot tubes into hydrogen and *diphenyl sulphide*,  $\begin{array}{l} C_6H_4 \\ | \\ C_6H_4 \end{array}\!\!>S$, colourless needles melting at 97°.

Cœroulignone, $C_{16}H_{16}O_6$, is a blue substance insoluble in alcohol and ether, obtained during the purification of raw pyroligneous acid, and which is precipitated from its phenol solution by alcohol in brilliant steel blue needles. It is converted by hydric sulphide or by zinc and hydrochloric acid into *hydrocœroulignone*, $C_{16}H_{18}O_6$, which further, by heating with hydrochloric acid to 200°, yields methyl chloride and hexahydroxy-diphenyl, of which body hydrocœroulignone is the tetramethyl ether. The reaction is represented by the equation:

$$C_{12}H_4(OH)_2(O.CH_3)_4 + 4HCl = 4CH_3Cl + C_{12}H_4(OH)_6.$$

Hexahydroxy-diphenyl crystallises in silvery plates, soluble in water, alcohol, and ether. It produces a beautiful blue violet colour with dilute potash solution.

With acetic anhydride a hexacetate is formed:

$$C_{12}H_4(O.C_2H_3O)_6,$$

crystallising in prisms melting at 145°. Heated with zinc dust it is reduced to diphenyl:

$$C_{12}H_4(OH)_6 + 6Zn = 6ZnO + C_{12}H_{10}.$$

Hydrocarbons, $C_{13}H_{12}$, *and their Derivatives.*

1145. *Diphenyl methane*, $C_{13}H_{12} = C_6H_5.CH_2.C_6H_5$, or *methene diphenyl*, is prepared synthetically by the action of 4 parts zinc dust on 10 parts benzyl chloride and 6 parts benzene at a gentle heat:

$$C_6H_5.CH_2Cl + C_6H_6 = HCl + C_6H_5.CH_2.C_6H_5\ ;$$

also by allowing a mixture of methylal (§ 403), benzene, acetic and concentrated sulphuric acids to stand for some time together:

$$CH_2(O.CH_3)_2 + 2C_6H_6 + 4H_2SO_4 = 2CH_3.HSO_4 + 2H_4SO_5 \\ + CH_2(C_6H_5)_2\ ;$$

or by the action of sulphuric acid on benzylic alcohol:

$$C_6H_5.CH_2.OH + C_6H_6 + H_2SO_4 = C_6H_5.CH_2.C_6H_5 + H_4SO_5,$$

and further by the reduction of some of its oxy-derivatives.

Diphenyl methane smells like oranges, crystallises in needles, melts between 26° and 27°, and boils at 261°–262°.

1146. *Hydroxy-diphenyl Methane.*—*a. Benzyl phenol:*

$$C_{13}H_{12}O = C_6H_5.CH_2.C_6H_4.OH,$$

is obtained similarly to diphenyl methane by heating benzyl chloride, phenol, and zinc dust. It crystallises in silvery needles melting at 84°, cannot be distilled without decomposition, and is not easily soluble in water.

β. Isomeric with *a* is the secondary alcohol, *diphenyl carbinol*, or *benzhydrol*, $C_6H_5.CH(OH).C_6H_2$, the result of the action of sodium amalgam on a weak alcoholic solution of benzophenone (comp. § 160).

It crystallises in silky needles, difficultly soluble in water, melting at 68°, and boiling (with partial decomposition into water and *benzhydro-ether*, $(C_6H_5)_2CH.O.CH(C_6H_5)_2)$ at 297°–298°. Oxidising agents reform benzophenone. By continued boiling with acetic acid *benzhydrol acetate*, $(C_6H_5)_2.CH.O.C_2H_3O$, a viscid liquid boiling at 301°–302°, is produced.

1147. *Benzophenone*, or *diphenyl ketone:*

$$C_{13}H_{10}O = C_6H_5.CO.C_6H_5,$$

is obtained, together with benzene, as a product of the dry distillation of calcium benzoate (comp. § 435) by heating mercury diphenyl and chlor-benzoyl:

$$(C_6H_5)_2Hg + ClCO.C_6H_5 = C_6H_5.HgCl + C_6H_5.CO.C_6H_5,$$

by the oxidation of diphenyl methane and benzhydrol with CrO_3 and dilute sulphuric acid, and by heating benzoic acid, benzene, and phosphoric anhydride for several hours at 200°:

$$C_6H_5.CO.OH + C_6H_6 + P_2O_5 = 2HPO_3 + C_6H_5.CO.C_6H_5.$$

It crystallises in large rhombic prisms soluble in alcohol, insoluble in water, melting between 48° and 49°, often solidifying to rhombohedra of 26°–27° melting point, which, however, gradually pass into the other modification.

Benzophenone heated with phosphoric chloride produces *diphenyl carbon dichloride*, $(C_6H_5)_2:CCl_2$, a liquid boiling with partial decomposition at 305°.

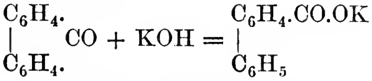
A further derivative of this group in *dimeth-oxyphenyl methane*, $CH_2\begin{array}{l}.C_6H_4.O.CH_3\\ .C_6H_4.O.CH_3\end{array}$, is prepared from methylal, anisol, and sulphuric acid; it melts at 52° and distils at about 360°.

1148. *Phenyl toluene*, $C_{13}H_{12} = C_6H_5.C_6H_4.CH_3$. One of the three isomers of this body is obtained by the action of sodium on a mixture of brom-benzene and orthobrom-toluene as a thick oil boiling at 300°.

The following two phenyl phenylene carbonic acids, $C_{13}H_{10}O_2$, are derivable from the phenyl toluenes.

1. *Paradiphenyl-carbonic acid*, $C_6H_5.C_6H_4.CO.OH$. Phenyl phenylene sulphonate of potassium yields by dry distillation with potassic cyanide *cyandiphenyl*, $C_6H_5.C_6H_4.CN$, in the form of a crystalline mass, insoluble in OH_2, melting at 84° or 85°. On boiling with alcoholic potash it gives ammonia and potassic paradiphenyl carbonate. The free acid forms grouped needle-shaped crystals of 219° melting point, subliming without decomposition. In acetic solution it is oxidised by chromic acid to terephthalic acid; distilled with lime it gives diphenyl. The barium and calcium salts are exceedingly insoluble in boiling water.

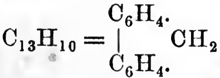
2. The isomeric *phenyl-benzoic acid*, obtained from diphenyl ketone by fusion with potash:



$$\begin{array}{l}C_6H_4.\\ \mid \\ C_6H_4.\end{array} CO + KOH = \begin{array}{l}C_6H_4.CO.OK\\ \mid \\ C_6H_5\end{array}$$

forms a colourless, branching crystalline mass, fusing at 110°–111° and giving a somewhat easily soluble calcium salt. By distillation with lime much diphenylene ketone is re-formed and very small amount of diphenyl.

Diphenylene ketone, $C_{12}H_8O$, results from the distillation of diphenic acid with lime. It separates from alcohol or ether solutions in large rhombic crystals, fusing at 84°, which yield *diphenylene methane*:



$$C_{13}H_{10} = \begin{array}{l}C_6H_4.\\ \mid \\ C_6H_4.\end{array} CH_2$$

on distillation over zinc dust.

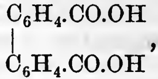
The same compound is found in that portion of coal tar distilling at 300°–305°. It may be purified by repeated crystallisations from alcohol, and then forms blue fluorescent plates, therefore called *fluorene*. It fuses at 113° and distils at 304°–305°, and gives diphenyl ketone on oxidation.

It combines with nascent hydrogen to form *diphenylene carbinol*, $C_{13}H_9.OH = \begin{array}{l}C_6H_4.\\ \mid \\ C_6H_4.\end{array} CH.OH$, or *fluorene alcohol*, separating from alcohol in six-sided plates of fusing point 153°, and giving with acetic anhydride rhombic crystals of the acetate, melting at 75°, and also oxidising to diphenylene ketone.

The Hydrocarbons, $C_{14}H_{14}$, *and their Derivatives.*

1. *Ditolyl*, $CH_3.C_6H_4.C_6H_4.CH_3$.

1149. Ditolyl results from the debromination of parabrom-toluene by means of sodium, so that the methyl groups must be in the para position. It crystallises in monoclinic prisms, somewhat freely soluble in hot alcohol and fusing at 121°.

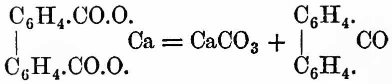


Diphenylene dicarbonic acid, $C_{14}H_{10}O_4 = \begin{array}{l} C_6H_4.CO.OH \\ | \\ C_6H_4.CO.OH \end{array}$, is doubtless a derivative of ditolyl, although not yet directly obtained from it.

It has been prepared from diphenylene disulphonic acid (§ 1144) by distilling its potassium salt with potassic cyanide and heating the *diphenylene dicyanide*, $C_{12}H_8(CN)_2$ (needles melting at 234°), produced to 180° with concentrated hydrochloric acid.

The free acid (which is doubtless the para compound) is a white powder, infusible, insoluble in water, alcohol, and ether, and cannot be sublimed. It gives an insoluble barium salt, and yields diphenyl on distillation with lime.

The isomeric *diphenic acid*, probably the ortho compound, results from the oxidation of phenanthrene with chromic acid. It forms needles somewhat soluble in hot water, easily in alcohol and ether, and melting at 226°, and yielding *principally* diphenylene ketone on heating with lime:



$$\begin{array}{l} C_6H_4.CO.O. \\ | \\ C_6H_4.CO.O. \end{array} Ca = CaCO_3 + \begin{array}{l} C_6H_4. \\ | \\ C_6H_4. \end{array} CO$$

Its barium salt, $C_{14}H_8BaO_4 + 4OH_2$, is easily soluble in water and crystallises well.

2. *Benzyl Toluene*, $C_6H_5.CH_2.C_6H_4.CH_3$.

1150. A mixture of hydrocarbons of this formula is obtained, similarly to diphenyl methane (§ 1145), by heating benzyl chloride with toluene and zinc dust:

$$C_6H_5.CH_2Cl + C_6H_5.CH_3 = HCl + C_6H_5.CH_2.C_6H_4.CH_3;$$

also by the action of iodine on toluene at 250°, and by heating benzyl chloride and water at 190°. The individual hydrocarbons of this mixture cannot be separated by distillation, as the mixture boils constantly at 279°, and no solid body is deposited even on cooling to $-30°$.

By the oxidation of the mixture phenyl-tolyl ketones are first formed, and later the two benzoyl benzoic acids.

Phenyl-tolyl ketones, $C_6H_5.CO.C_6H_4.CH_3$. At least two compounds of this formula result from the oxidation of the benzyl toluenes, as also by heating benzoic acid and toluene with phosphoric anhydride (§ 1147) and by the dry distillation of a mixture of calcium benzoate and paratoluate. From the oily mixture of products the *phenyl-paratolyl ketone* is separated by cooling in colourless prisms, melting at 56°–57°, boiling at 313°–314°, little soluble in alcohol. Heated to 250° with soda lime, benzene distils over and sodium para-toluate is formed:

$$C_6H_5.CO.C_6H_4.CH_3 + NaOH = C_6H_6 + NaO.CO.C_6H_4.CH_3.$$

The liquid bodies formed at the same time as the phenyl-paratolyl ketone have not as yet been separated in a pure state.

1151. *Benzoyl benzoic acids*, $C_{14}H_{10}O_3 = C_6H_5.CO.C_6H_4.CO.OH$, obtained from the benzyl toluene mixture or the ketones just described, may be separated by means of cold water.

(1) *Parabenzoyl benzoic acid,* prepared from solid phenytolyl ketone, is almost insoluble in cold water, crystallises in thin shining plates, fusing point 194°, which may be sublimed.

Nascent hydrogen in alcoholic solution converts it into *benzhydryl benzoic acid*, $C_{14}H_{12}O_3 = C_6H_5.CH(OH).C_6H_4.CO.OH$, crystallising in radiating grouped needles of melting point 164°–165°, easily soluble in boiling water. Heated with hydriodic acid to 160° it is reduced to *benzyl benzoic acid*, $C_{10}H_{12}O_2 = C_6H_5.CH_2.C_6H_4.CO.OH$, needles or plates melting at 155°.

(2) *β-Benzoyl benzoic acid* solidifies from water in broad needles of the formula $C_{14}H_{10}O_3,2OH_2$, which, when hydrated, melt at 85° or 87°, when anhydrous at 127°–128°.

3. *Dibenzyl*, $C_6H_5.CH_2.CH_2.C_6H_5$.

1152. Dibenzyl is obtained by the dechlorination of benzyl chloride by sodium in large colourless prisms melting at 52° and boiling at 284°. It is easily soluble in alcohol.

The same hydrocarbon group is contained in stilbene, and probably also in tolane.

Stilbene, $C_{14}H_{12} = C_6H_5.CH : CH.C_6H_5$, or toluylene. is prepared by passing the vapours of toluene or of dibenzyl over heated plumbic oxide:

$$C_6H_5.CH_2.CH_2.C_6H_5 + PbO = Pb + OH_2 + C_6H_5.CH : CH.C_6H_5,$$

by the action of sodium on benzoic aldehyde, and by some reactions of the oxygen derivatives of dibenzyl, yet to be described.

It crystallises from its hot alcoholic saturated solution on cooling in large thin colourless plates, melting at 120° and boiling between 306° and 307°. Heating with hydriodic acid converts it into dibenzyl:

$$C_6H_5.CH:CH.C_6H_5 + 2HI = I_2 + C_6H_5.CH_2.CH_2.C_6H_5.$$

Chromic acid oxidises it to benzaldehyde and benzoic acid. It combines with bromine to form a crystalline *stilbene dibromide:*

$$C_6H_5.CHBr.CHBr.C_6H_5,$$

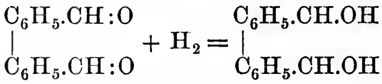
which is converted by alcoholic potash first into *monobrom-stilbene*, $C_6H_5.CH:CBr.C_6H_5$, and finally into

Tolane, $C_{14}H_{10}$ ($= C_6H_5.C : C.C_6H_5$?), which separates from alcohol or ether solution in colourless crystals melting at 60°, and giving with bromine two isomeric dibromides, $C_{14}H_{10}Br_2$, α in scaly crystals melting between 200° and 205°, and β crystallising in needles and melting at 64°. (For tolane chlorides see under benzil, § 1154.)

1153. *Hydroxyl derivatives of dibenzyl* are obtained from the ketone derivatives or from benzaldehyde by nascent hydrogen.

Toluylene hydrate, $C_{14}H_{14}O = C_6H_5.CH_2.CH(OH).C_6H_5$, is obtained by the action of nascent hydrogen on desoxybenzoïn, and therefore also from benzoïn, in alcoholic solution. It crystallises in long brittle needles of 62° fusing point, insoluble in water, but dissolving in alcohol and ether, and giving with chlor-acetyl a thick liquid acetate, $C_{14}H_{13}.O.C_2H_3O$. On boiling with dilute sulphuric acid it splits up into water and stilbene.

Hydro-benzoïn, $C_{14}H_{14}O_2 = C_6H_5.CH(OH).CH(OH).C_6H_5$, is prepared from benzoïn by the agency of nascent hydrogen or alcoholic potash, also along with the following substances by the treatment of benzaldehyde with sodium amalgam or zinc and hydrochloric acid :



$$\begin{array}{l} C_6H_5.CH:O \\ | \\ C_6H_5.CH:O \end{array} + H_2 = \begin{array}{l} C_6H_5.CH.OH \\ | \\ C_6H_5.CH.OH \end{array}$$

It crystallises in rhombic tables of 132·5° melting point, not dissolving easily in water. With chlor-acetyl it gives a diacetate :

$$C_{14}H_{12}(O.C_2H_3O)_2,$$

crystallising in prisms of 134° melting point. Phosphorus pentachloride gives *stilbene dichloride,* $C_{14}H_{12}Cl_2$. Nitric acid reproduces benzoïn by oxidation.

The isomeric *isohydro-benzoïn* is also formed by the action of sodium amalgam on benzaldehyde solution in alcohol. It crystallises from water in efflorescent prisms, from alcohol anhydrous in hexagonal forms, melting at 119·5°. It is more readily soluble in alcohol than hydro-benzoïn. Its diacetate forms plates of 117°–118° melting point.

Isohydro-benzoïn also yields benzaldehyde on oxidation, and hence appears to have the same constitution as benzoïn.

1154. *Ketonic Derivatives of Dibenzyl.*—1. *Desoxybenzoïn :*

$$C_{14}H_{12}O = C_6H_5.CO.CH_2.C_6H_5,$$

or *phenyl-benzyl ketone,* results along with hydro-benzoïn and toluylene hydrate from the action of zinc and HCl on an alcoholic solution of benzoïn ; also by heating brom-stilbene with water to 180°, by oxidation of toluylene hydrate with dilute nitric acid, and by dry distillation of a mixture of calcic phenyl acetate and benzoate.

It crystallises from alcohol in large colourless tables, melting at 55°, which when treated with phosphoric chloride give hydrochloric acid and monchlor-stilbene. With hydriodic acid at a high temperature dibenzyl is produced.

2. *Benzoïn,* $C_{14}H_{12}O_2 = C_6H_5.CO.CH(OH).C_6H_5$, is prepared by gently warming hydro-benzoïn with concentrated nitric acid, and by the action of an alcoholic potassic cyanide solution on benzaldehyde :

$$2C_6H_5.CH:O = C_6H_5.CO.CH(OH).C_6H_5.$$

It forms colourless prisms of 133°–134° melting point, difficultly soluble in water, alcohol, and ether, and gives an acetate, $C_{14}H_{11}(O.C_2H_3O)O$, with chlor-acetyl.

Chromic acid produces benzaldehyde and benzoic acid:

$$C_6H_5.CO.CH(OH).C_6H_5 + O = C_6H_5.CO.OH + CHO.C_6H_5.$$

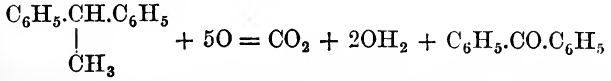
3. *Benzil*, $C_{14}H_{10}O_2 = C_6H_5.CO.CO.C_6H_5$, is the product of the oxidation of benzoïn with nitric acid, and is also obtained by heating stilbene dibromide with water and silver oxide to 200°, tolane being simultaneously produced. It separates from alcohol in six-sided prisms of 90° melting point, which are quite insoluble in water. Chromic and sulphuric acids oxidise it completely to benzoic acid. Nascent hydrogen reproduces benzoïn. Phosphoric chloride at a gentle heat gives chlor-benzil, $C_6H_5.CCl_2.CO.C_6H_5$; at 200° tolane tetrachloride, $C_6H_5.CCl_2.CCl_2.C_6H_5$. The former crystallises in rhombic prisms and tables of fusing point 71°, which are reduced by zinc and hydrochloric acid to desoxybenzoïn; the latter is also crystalline and gives tolane with sodium amalgam.

4. *Diphenyl Ethane*, $(C_6H_5)_2.CH.CH_3$.

1155. This hydrocarbon can be prepared, analogously to the production of diphenyl methane from methyl aldehyde and benzene, by the action of ethyl aldehyde on benzene:

$$2C_6H_6 + COH.CH_3 = OH_2 + (C_6H_5)_2.CH.CH_3.$$

The best mode of procedure is to gradually mix 1 part of paraldehyde with 100 parts of concentrated sulphuric acid and then add the benzene. The tarry-looking substance precipitated by water is washed out with ether and the latter fractionally distilled. Diphenyl ethane is a colourless liquid boiling at 270°, and solidifying under 0°. Chloral and bromal, treated in similar manner, yield *diphenyl trichlor-ethane*, $(C_6H_5)_2:CH.CCl_3$, and *diphenyl tribrom-ethane*, $(C_6H_5)_2:CH.CBr_3$, both being crystalline and melting respectively at 64° and 89°. By the long-continued action of sodium amalgam on the alcoholic solutions of both substances, and heating this product to 210° with hydriodic acid and amorphous phosphorus, diphenyl ethane is produced, which is oxidised by chromic acid to diphenyl ketone:



$$\begin{array}{l} C_6H_5.CH.C_6H_5 \\ \qquad\; | \\ \qquad CH_3 \end{array} + 5O = CO_2 + 2OH_2 + C_6H_5.CO.C_6H_5$$

A mixture of monochlor-aldehyde (§ 652) and benzene by addition of sulphuric acid is converted into *diphenyl chlor-ethane*:

$$(C_6H_5)_2:CH.CH_2Cl,$$

with liberation of hydrogen. It has not yet been isolated in the pure state, but by boiling with alcoholic potash gives

Diphenyl ethylene, $C_{14}H_{12} = (C_6H_5)_2:C:CH_2$, a colourless, agreeably smelling oil of 277° boiling point, easily oxidisable to CO_2, OH_2, and diphenyl ketone. By dry distillation hydrochloric acid is eliminated, whilst an internal molecular change takes place, by which the diphenyl ethylene passes into the isomeric body *stilbene* (§ 1151):

$$\begin{array}{l} C_6H_5. \\ C_6H_5. \end{array} CH.CH_2Cl = HCl + \begin{array}{l} C_6H_5.CH \\ \qquad | \\ C_6H_5.CH \end{array}$$

Diphenylene-hydrate-trichlor-ethane, $(HO.C_6H_4)_2{:}CH.CCl_3$, is formed by the action of strong sulphuric acid on a mixture of chloral and phenol. It crystallises from a mixture of benzene and alcohol in white crystals, which decompose at their melting point, 202°. The alcoholic solution boiled with zinc dust gives *diphenylene-hydrate-ethylene*, $C_{14}H_{12}O_2 = (HO.C_6H_4)_2{:}C{:}CH_2$, the crystals of which are small and decompose when melting at 280°.

1156. The two following acids may both be considered to be derived from the carbon nucleus of diphenyl ethane:—

Diphenyl acetic acid, $C_{14}H_{12}O_2 = (C_6H_5)_2{:}CH.CO.OH$, isomeric with benzyl benzoic acid (§ 1151), obtained by heating phenyl-brom-acetic acid (§ 1081) with zinc dust and benzene:

$$C_6H_5.CHBr.CO.OH + C_6H_6 = HCl + (C_6H_5)_2{:}CH.CO.OH,$$

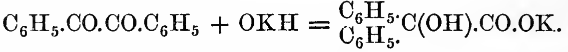
and by the reduction of benzylic acid with hydric iodide, crystallises from hot aqueous solutions in fine needles, from alcohol in leafy crystals, melting at 140° and decomposing on sublimation. Its ethyl salt, $(C_6H_5)_2{:}CH.CO.O.C_2H_5$, crystallises in prisms, melting at 57°–58°; the easily soluble barium salt, $(C_{14}H_{11}O_2)_2Ba + 2OH_2$, in grouped needles. Both the acid and its salts yield diphenyl methane on dry distillation:

$$(C_6H_5)_2{:}CH.CO.OH = CO_2 + (C_6H_5)_2{:}CH_2.$$

Diphenyl glycolic acid, or *benzilic acid*:

$$C_{14}H_{12}O_3 = (C_6H_5)_2.C(OH).CO.OH,$$

isomeric with benzyl-hydryl benzoic acid (§ 1151, 1), results from an intermolecular change on heating benzil (§ 1154) with excess of alcoholic potash solution until the violet colour of the solution has passed into bright yellow:



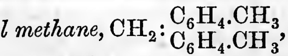
$$C_6H_5.CO.CO.C_6H_5 + OKH = \genfrac{}{}{0pt}{}{C_6H_5.}{C_6H_5.}C(OH).CO.OK.$$

Fused diphenyl-acetic acid is converted by bromine vapour into *diphenyl-brom-acetic acid*, $(C_6H_5)_2CBr.CO.OH$, which by long boiling with water yields benzilic acid and hydric bromide.

Benzilic acid crystallises in monoclinic prisms, melting at 150°, soluble in hot water and alcohol. At a high temperature, and also by warming with hydric sulphate, it becomes coloured deep red, and gives on oxidation diphenyl ketone. Hydric iodide reduces it on heating to diphenyl acetic acid (comp. § 706), and when distilled with baric hydrate benzhydrol (§ 1143, 2) is produced.

Hydrocarbons, $C_{15}H_{16}$, *and their Derivatives.*

1157. 1. *Benzyl-ethyl benzene*, $C_6H_5.CH_2.C_6H_4.C_2H_5$, is obtained by heating benzyl bromide and ethyl benzene with zinc dust as an oil boiling between 294° and 295°.



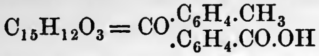
2. *Ditolyl methane*, $CH_2{:}\genfrac{}{}{0pt}{}{C_6H_4.CH_3}{C_6H_4.CH_3}$, results from the dehydrating action of sulphuric acid on a mixture of methylal and toluene (§ 1145). It is a blue fluorescing oil of agreeable smell, boiling at 290°, which by careful oxidation yields *ditolyl ketone*:

$$C_{15}H_{14}O = (CH_3.C_6H_4)_2{:}CO,$$

crystallising in rhombic crystals, soluble in alcohol, insoluble in water, and combining with nascent hydrogen to form *ditolyl carbinol:*

$$C_{15}H_{16}O = (CH_3.C_6H_4)_2:CH(OH),$$

in fibrous crystals, melting at 69°. Ditolyl ketone on further oxidation yields *tolyl ketone benzoic acid*:



$$C_{15}H_{12}O_3 = CO\begin{matrix}.C_6H_4.CH_3\\.C_6H_4.CO.OH\end{matrix}$$

It fuses at 222° and forms fine needles difficultly soluble in alcohol.

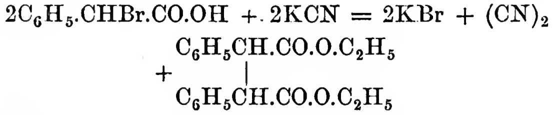
3. *Dibenzyl ketone,* $(C_6H_5.CH_2)_2CO$, is isomeric with ditolyl ketone, and may be regarded as derived from the as yet unknown hydrocarbon $C_6H_5.CH_2.CH_2.CH_2.C_6H_5$; it is obtained by the dry distillation of calcic phenyl-acetate, and is a crystalline body melting at 30° and boiling between 320° and 321°.

1158. A short description of the higher homologues of this group will suffice.

Ditolyl ethane, $C_{16}H_{18} = (CH_3.C_6H_4)_2:CH.CH_3$, prepared from para-aldehyde, toluol, and hydric sulphate, is an oil boiling at 295°–298°, which gives on oxidation water, carbonic anhydride, and ditolyl ketone.

Dimesityl methane, $C_{19}H_{24} = [(CH_3)_3 : C_6H_2]_2 : CH_2$, obtained from methylal and mesitylene by heating with hydric sulphate, crystallises in large colourless monoclinic prisms of fusing point 130°.

Dibenzyl dicarbonic acid, or *diphenyl succinic acid,* $C_{16}H_{14}O_4$, may be described in this group; it is obtained as its ethyl salt by long-continued heating of ethylic phenyl-brom-acetate with alcohol and KCN at 100°:



$$2C_6H_5.CHBr.CO.OH + 2KCN = 2KBr + (CN)_2 + \begin{matrix}C_6H_5CH.CO.O.C_2H_5\\|\\C_6H_5CH.CO.O.C_2H_5\end{matrix}$$

On saponifying the ethylic salt with potassic hydrate and neutralising with hydrochloric acid the free acid is obtained. It forms colourless, hard, difficultly soluble prisms of the formula $C_{16}H_{14}O_4 + OH_2$, fusing first at 182°, then solidifying and again melting at 222°. On distillation with lime dibenzyl and stilbene are produced.

Anthracene and its Derivatives.

1159. *Anthracene,* $C_{14}H_{10} = C_6H_4\begin{matrix}.CH.\\.CH.\end{matrix}C_6H_4$, is a large constituent of the high boiling portions of coal-tar oil, from which it is obtained by repeated distillation and recrystallisation of the solid fractions from benzene. As this method always yields a yellow-coloured product it is further sublimed at as low a temperature as possible in a rapid stream of air, and finally bleached by exposure to sunlight in solution in benzene. The colourless solution after filtration from para-anthracene yields, on evaporation of the solvent, pure anthracene.

Many synthetic methods for the production of anthracene are known. Amongst others may be mentioned passing the vapour of toluene through strongly heated tubes filled with pumice or plumbic oxide:

$$2C_6H_5.CH_3 = 3H_2 + C_6H_4{:}C_2H_2{:}C_6H_4\,;$$

by heating phenyl-tolyl ketone (liquid) (§ 1150) with zinc dust:

$$C_6H_5.CO.C_6H_4.CH_3 + Zn = ZnO + H_2 + C_{14}H_{10}\,;$$

and from benzyl chloride (§ 1027) by heating with water to 190°. By this reaction, however, a number of products are formed, which by distillation give anthracene along with benzyl toluene, benzyl ether, &c. Anthracene is finally obtained by the distillation of all its derivatives over heated zinc dust.

Perfectly pure anthracene crystallises in colourless rhombic tables having a magnificent blue fluorescence. It melts at 213° and boils somewhat over 360°. It is totally insoluble in water and only very slightly so in alcohol and ether. Warm benzene dissolves it more readily.

When concentrated solutions of anthracene and trinitro-phenol are mixed beautiful red needles of the compound

$$C_{14}H_{10},2C_6H_2(NO_2)_3.OH$$

separate.

Para-anthracene, isomeric or polymeric with anthracene, separates from the solutions of the latter when exposed to sunlight. It differs from anthracene by its insolubility in benzene, its greater stability, and complete resistance to the action of bromine or concentrated nitric acid. It melts at 244°, being at the same time converted into ordinary anthracene.

1160. *Hydrides of Anthracene.*—These compounds may be obtained by heating anthracene with hydric iodide and phosphorus. At a temperature of 160°–170° *anthracene dihydride*, $C_{14}H_{12}$, is produced, the same body being also formed when anthracene is heated with sodium amalgam and alcohol for a long time. This substance crystallises in small colourless monoclinic tables, which dissolve easily in alcohol and ether, melt at 106°, and boil at 305°. At a red heat it is again broken up into anthracene and hydrogen; also by heating with concentrated hydric sulphate, with reduction of the latter to sulphite. By very long continued heating of anthracene with hydric iodide and phosphorus to about 220° *anthracene hexahydride*, $C_{14}H_{16}$, is produced, which also forms leafy crystals, easily soluble in alcohol and ether, melting at 63°, and boiling at 290°. It behaves similarly to the dihydride when heated with sulphuric acid.

1161. *Halogen Derivatives of Anthracene.*—Chlorine and bromine form both addition and substitution products with anthracene. Chlorine, for instance, forms in the first instance an *anthracene dichloride*, $C_{14}H_{10}Cl_2$, crystallising in long needles, from which alcoholic potash removes one atom of chlorine, yielding *monochlor-anthracene*, small scaly crystals resulting. The same body also results from heating anthracene in a stream of chlorine gas. Other chlor-substitution products, $C_{14}H_8Cl_2$ and $C_{14}H_6Cl_4$, crystallise in yellow needles, of 209° and 220° melting points respectively.

On adding bromine to a solution of anthracene in sulphide of carbon the sole product is *dibrom-anthracene*, $C_{14}H_8Br_2$, golden yellow needles melting at 221°, which on heating with alcoholic potash to 160° is reduced to anthracene with simultaneous oxidation of the alcohol. Dibrom-anthracene combines directly with bromine to form *dibrom-anthracene tetrabromide*, $C_{14}H_8Br_6$, the same body being also formed by the action of bromine vapour on finely divided anthracene. It crystallises in colourless tables, which melt between 170° and 180°, decomposing at the same time into *tribrom-anthracene*:

$$C_{14}H_7Br_3,$$

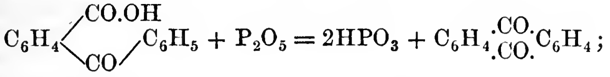
yellow volatile needles, melting at 169°. Dibrom-anthracene tetrabromide heated with alcoholic potash yields *tetrabrom-anthracene*, $C_{14}H_6Br_4$, melting at 254°.

Oxygen Derivatives of Anthracene.

1162. *Anthraquinone*, $C_{14}H_8O_2 = C_6H_4{\substack{.CO.\\ .CO.}}C_6H_4$. The best method for the preparation of anthraquinone is by oxidation of anthracene dissolved in glacial acetic acid with potassic dichromate. Nitric acid and dichlor- or dibrom-anthracene may also be used.

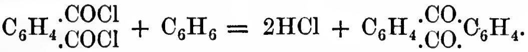
Conclusive proofs of the constitution of anthraquinone as a double ketone are furnished by its synthetical methods of preparation. For instance--

Liquid phenyl-tolyl ketone passed in a state of vapour over heated plumbic oxide yields anthraquinone; it is also obtained by heating β-benzoyl benzoic acid (§ 1151) with phosphoric anhydride to 200°:



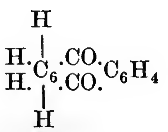
$$C_6H_4\left\langle\substack{CO.OH\\ CO}\right\rangle C_6H_5 + P_2O_5 = 2HPO_3 + C_6H_4{\substack{.CO.\\ .CO.}}C_6H_4;$$

by heating phthalyl dichloride to 220° with benzene and zinc dust:



$$C_6H_4{\substack{.COCl\\ .COCl}} + C_6H_6 = 2HCl + C_6H_4{\substack{.CO.\\ .CO.}}C_6H_4.$$

From its formation from phthalyl dichloride it seems pretty conclusive that the CO groups are in the ortho position to at least one of the benzene groups:

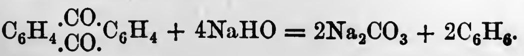


$$\begin{matrix} & H & & \\ H. & | & .CO. & \\ & C_6 & & C_6H_4 \\ H. & | & .CO. & \\ & H & & \end{matrix}$$

After being sublimed anthraquinone forms brilliant yellow needles, melting at 273°, which are easily soluble in hot benzene, only slightly so in cold benzene, or alcohol, or ether. It is reduced by heating with hydric iodide, phosphonium iodide, or zinc dust, to anthracene. Potash, when heated with it to 250°, splits it up into benzoic acid:

$$C_6H_4{\substack{.CO.\\ .CO.}}C_6H_4 + 2KOH = 2C_6H_5.CO.OK.$$

Distilled with soda lime it yields benzene:

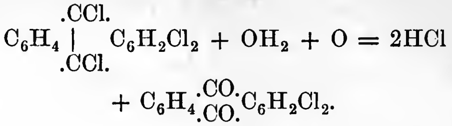


$$C_6H_4{\substack{.CO.\\ .CO.}}C_6H_4 + 4NaHO = 2Na_2CO_3 + 2C_6H_6.$$

Phosphoric pentachloride gives a mixture of tri- and tetra-chlor-anthracene.

Anthrahydroquinone, $C_6H_4\genfrac{}{}{0pt}{}{.CH(OH)}{.CO}:C_6H_4$, is obtained, by warming anthraquinone with zinc dust and caustic potash, and neutralising its yellow solution with HCl, as a yellow substance which re-oxidises on exposure to the air in a moist state.

1163. *Halogen Substitution Products of Anthraquinone.*—Tetrachlor-anthracene gives, on oxidation, yellow needles of *dichlor-anthraquinone :*



$$C_6H_4\genfrac{}{}{0pt}{}{.CCl.}{.CCl.}\Big| \; C_6H_2Cl_2 + OH_2 + O = 2HCl$$
$$+ C_6H_4\genfrac{}{}{0pt}{}{.CO.}{.CO.}C_6H_2Cl_2.$$

Similarly on oxidation tribrom-anthracene gives colourless needles of brom-anthraquinone, melting at 187° ; and tetrabrom-anthracene yields *dibrom-anthraquinone*, $C_{14}H_6Br_2O_2$. The latter may also be formed by heating anthraquinone with two molecules of bromine at 100°. It crystallises in bright yellow needles, which may be sublimed.

1164. *Nitro- and Amido-Anthraquinones.*—*Nitro-anthraquinone*, $C_{14}H_7(NO_2)O_2$, is obtained by boiling a solution of anthraquinone in the strongest nitric acid, as a bright yellow powder, melting at 230° and subliming in needles. It is only easily soluble in glacial acetic acid. On warming with a solution of potassium thiohydrate it is reduced to *amido-anthraquinone*, $C_{14}H_7(NH_2)O_2$, a vermilion red powder, melting at 256°, which dissolves in acetic acid, but does not form salts with mineral acids.

In the preparation of anthraquinone by warming anthracene with dilute nitric acid a small quantity of *dinitro-anthraquinone :*

$$C_{14}H_6(NO_2)_2O_2,$$

is also produced, and may be separated from the anthraquinone by its less solubility in alcohol.

Isodinitro-anthraquinone, obtained by warming anthraquinone and nitro-anthraquinone with nitro-sulphuric acid, crystallises from chloroform in small bright yellow monclinic prisms, which soften at 252° and sublime undecomposed at a higher temperature. Tin and hydrochloric acid reduce it to *isodiamido-anthraquinone :*

$$C_{14}H_6.(NH_2)_2O_2,$$

melting at 236° and forming red needles, which dissolve in strong acids and is reprecipitated unchanged on dilution.

1165. *Anthraquinone Sulphonic Acids.*—By heating anthraquinone with twice its weight of sulphuric acid to 250° *anthraquinone sulphonic acid* is produced, $C_{14}H_7(SO_3H)O_2$. Similarly treated with four to five times its weight of sulphuric acid, *anthraquinone disulphonic acid*, $C_{14}H_6(SO_3H)_2O_2$, results. Both acids are yellow crystalline bodies, soluble in water and alcohol, and give barium salts, the baric disulphonate, $C_{14}H_6O_2\genfrac{}{}{0pt}{}{.SO_2.O}{.SO_2.O}Ba$, being easily soluble in water.

1166. *Hydroxy-anthraquinones*, $C_{14}H_8O_3 = C_{14}H_7.(OH).O_2$. Two isomers are known.

1. *Oxyanthraquinone* is formed by careful fusion of brom-anthraquinone or anthraquinone sulphonic acid with potash :

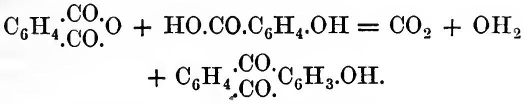
$$C_{14}H_7(SO_2.OK)O_2 + 2KOH = K_2SO_3 + OH_2 + C_{14}H_7(OK)O_2.$$

Potassic alizarate easily results from the further action of the potash :

$$C_{14}H_7(OK)O_2 + OKH = C_{14}H_6(OK)_2O_2 + H_2.$$

On treating with dilute HCl a mixture of alizarine and oxyanthraquinone is precipitated, which on boiling with $BaCO_3$ is converted into the barium derivatives of the two bodies. That of oxyanthraquinone being soluble, it is easily separated from the alizarine by solution and subsequent decomposition with HCl.

Amido-anthraquinone is converted by treatment with nitrous acid and subsequent boiling of the product, diazo-anthraquinone, with water into oxyanthraquinone. Synthetically oxyanthraquinone is obtained by heating phthalic anhydride with salicylic acid and sulphuric acid :



$$C_6H_4{\begin{smallmatrix}.CO.\\.CO.\end{smallmatrix}}O + HO.CO.C_6H_4.OH = CO_2 + OH_2 + C_6H_4{\begin{smallmatrix}.CO.\\.CO.\end{smallmatrix}}C_6H_3.OH.$$

It crystallises in yellow needles or plates, melting between 268° and 271°, and may be sublimed. It gives with the alkalies and alkaline earths soluble red or red-brown compounds; with acetic anhydride a colourless acetate, $C_{14}H_7(O.C_2H_3O)O_2$, which crystallises in needles and melts at 158°.

2. By heating phthalic anhydride with phenol and sulphuric acid to a high temperature (§ 1175) a mixture of oxyanthraquinone with an isomeric *erythro-oxyanthraquinone* is produced; the latter body is precipitated by water in yellow flocks. Erythro-oxyanthraquinone forms *insoluble* compounds with baric and calcic hydrates, which are decomposed by carbonic acid, by which means it is easily separated from oxyanthraquinone.

Erythro-oxyanthraquinone crystallises in orange yellow needles, melting between 173° and 180°, and sublimes at about 150°.

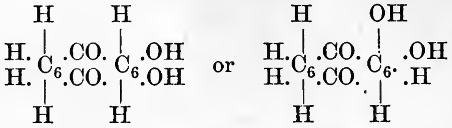
1167. *Dihydroxy-anthraquinones*, $C_{14}H_6(OH)_2O_2$. Several isomers of this formula are known in which the two hydroxyl groups may be combined to one or divided between the two phenyl groups. The constitution of several of these isomers is quite unknown; they are, however, all reduced to anthracene at a high temperature by zinc dust.

1. *Alizarine.*—Alizarine is obtained as a potassium compound by heating disubstituted anthraquinones—dichlor-, dibrom-anthraquinone, and anthraquinone disulphonic acid—with caustic potash to 250°–270° :

$$C_{14}H_6(SO_2.OK)_2O_2 + 4OKH = 2SO_3K_2 + C_{14}H_6(OK)_2O_2 + 2OH_2;$$

and also from monosubstituted anthraquinones, which pass first into oxyanthraquinone; and finally by melting with potash into dihydroxy-anthraquinone (§ 1166). On dissolving the fused product in water and adding HCl alizarine is precipitated, and purified by sublimation or recrystallisation from alcohol. Erythro-oxyanthraquinone also yields alizarine when melted with potash.

The constitution of alizarine is shown by its synthesis from phthalic anhydride and pyrocatechin when heated with sulphuric acid to 140°. The brown liquid gives, on addition of water, a black precipitate, from which alizarine may be extracted by means of alcohol. Since pyrocatechin may be regarded as ortho-dihydroxy-benzene, one of the following two formulæ must represent alizarine:



$$\begin{array}{c} \mathrm{H}\qquad\mathrm{H} \\ \mathrm{H.}\,\mathrm{C_6}\begin{matrix}\mathrm{.CO.}\\ \mathrm{.CO.}\end{matrix}\mathrm{C_6}\begin{matrix}\mathrm{.OH}\\ \mathrm{.OH}\end{matrix} \\ \mathrm{H.} \\ \mathrm{H}\qquad\mathrm{H} \end{array} \quad \text{or} \quad \begin{array}{c} \mathrm{H}\qquad\mathrm{OH} \\ \mathrm{H.}\,\mathrm{C_6}\begin{matrix}\mathrm{.CO.}\\ \mathrm{.CO.}\end{matrix}\mathrm{C_6}\begin{matrix}\mathrm{.OH}\\ \mathrm{.H}\end{matrix} \\ \mathrm{H.} \\ \mathrm{H}\qquad\mathrm{H} \end{array}$$

and from its formation from both oxyanthraquinones very probably the latter one.

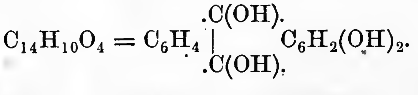
Alizarine crystallises from alcohol or ether in brownish yellow prisms containing water, which by drying become red; it melts at 215°, and can be sublimed by carefully heating in long red needles. It is slightly soluble in boiling water, more so in alcohol and ether.

Diaceto-alizarine, $C_{14}H_6(O.C_2H_3O)_2O_2$, is produced as a yellow powder on heating alizarine with acetic anhydride.

As a diphenol alizarine forms compounds with metals. It dissolves in potash to a fine purple colour, $C_{14}H_6(OK)_2O_2$. An alcoholic solution of alizarine gives blue precipitates with lime and baryta water, $C_{14}H_6(O_2Ca)O_2,OH_2$ and $C_{14}H_6(O_2Ba)O_2,OH_2$. Alkaline solutions of alizarine and alum give a beautiful red *lake*. Goods mordanted with alumina are dyed deep red with alizarine. Iron salts give a violet colour.

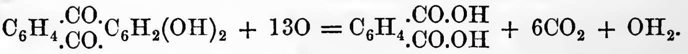
'Turkey red' is produced on cotton by mordanting with alum and oil and dyeing with alizarine.

On warming an alkaline alizarine solution with tin, the violet colour passes into yellowish red, and acids produce a precipitate of yellow *hydralizarine*, a dihydroxy-dihydranthraquinone:



$$C_{14}H_{10}O_4 = C_6H_4\begin{matrix}\mathrm{.C(OH).}\\ |\\ \mathrm{.C(OH).}\end{matrix}C_6H_2(OH)_2.$$

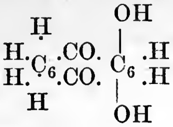
Alizarine is oxidised to phthalic acid on heating with nitric acid:



$$C_6H_4\begin{matrix}\mathrm{.CO.}\\ \mathrm{.CO.}\end{matrix}C_6H_2(OH)_2 + 13O = C_6H_4\begin{matrix}\mathrm{.CO.OH}\\ \mathrm{.CO.OH}\end{matrix} + 6CO_2 + OH_2.$$

Ruberythric acid can be extracted from fresh madder root by cold water. After precipitating other matters with normal plumbic acetate the filtrate is treated with basic plumbic acetate, to precipitate ruberythric acid. The red deposit is then decomposed by sulphuretted hydrogen and extracted with alcohol. Ruberythric acid crystallises in yellow prisms, which are readily soluble in hot water, alcohol, and ether; it is converted into sugar and alizarine by fermentive actions, acids, or alkalies.

2. *Quinizarine.*—Quinizarine is synthesised by heating phthalic anhydride with hydroquinone and sulphuric acid, precipitating the product with water, and extracting with benzene. The chlor-phenol, boiling at 218° (§ 988), may be used instead of hydroquinone. It crystallises from ether in yellow-red plates, from alcohol in needles, melts between 194° and 195°, and sublimes for the most part unchanged. It dissolves in alkalies to a pure blue solution. From its mode of formation the most probable constitution is:



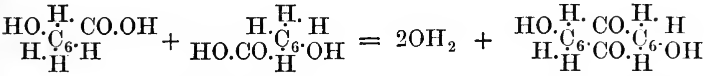
$$\overset{\text{H}}{\underset{\text{H}}{\begin{matrix}\text{H.}\\ \text{H.}\end{matrix}C_6}}\begin{matrix}\text{.CO.}\\ \text{.CO.}\end{matrix}\overset{\text{OH}}{\underset{\text{OH}}{C_6}}\begin{matrix}\text{.H}\\ \text{.H}\end{matrix}$$

3. *Anthraflavone* is often obtained in small quantities, together with alizarine, from the disubstituted anthraquinones. It is synthesised by heating metaoxybenzoic acid to 180° for many hours with hydric sulphate. The liquid yields, on dilution with water, a dark green precipitate, which is extracted with baric hydrate. After treating with animal charcoal the barium compound is decomposed with HCl and the dried precipitate extracted with ether.

Anthraflavone crystallises in yellow needles, which sublime partly undecomposed before melting at a temperature above 300°. It dissolves to brown solutions in alkalies and sulphuric acid, and gives a colourless diaceto compound with acetic anhydride:

$$C_{14}H_6(O.C_2H_3O.)_2O_2.$$

According to its formation each phenyl group contains a hydroxyl group:



$$\begin{matrix}\text{HO.}\\ \text{H.}\end{matrix}\overset{\text{H.}}{\underset{\text{H}}{C_6}}\begin{matrix}\text{CO.OH}\\ \text{.H}\end{matrix} + \begin{matrix}\text{H.}\\ \text{HO.CO.}\end{matrix}\overset{\text{H.}}{\underset{\text{H}}{C_6}}\begin{matrix}\text{H}\\ \text{.OH}\end{matrix} = 2OH_2 + \begin{matrix}\text{HO.}\\ \text{H.}\end{matrix}\overset{\text{H.}}{\underset{\text{H}}{C_6}}\begin{matrix}\text{CO.}\\ \text{CO.}\end{matrix}\overset{\text{H.}}{\underset{\text{H}}{C_6}}\begin{matrix}\text{H}\\ \text{.OH}\end{matrix}$$

Fused caustic potash splits it up into two molecules of *paraoxybenzoic acid.*

4. *Frangulic acid* is formed by the decomposition of its glucoside, frangulin, with mineral acids. It crystallises from alcohol in orange yellow quadratic plates or needles, $2C_{14}H_6(OH)_2O_2,3OH_2$, which only lose their water at 180° and melt between 252° and 254°. The diaceto compound forms brass yellow plates, melting at 184°.

The glucoside *frangulin* is isolated from the bark of *Rhamnus Frangula* by digestion with hot alcohol, and forms a yellow crystalline mass almost insoluble in water. It melts at 226°, dissolves to a red-coloured solution in alkalies, and is decomposed by dilute acids:

$$C_{20}H_{20}O_{10} = C_{14}H_8O_4 = C_6H_{12}O_6.$$

5. *Chrysophanic acid* (parietic or rheïnic acid) is found in senna leaves, in rhubarb root, in the root of *Rumex obtusifolia,* and in *Parmelia parietina,* from all of which it may be easily extracted by dilute potassic hydrate. Hydrochloric acid precipitates it from this solution in golden yellow prisms, which after recrystallisation from chloroform melt at 162°. It forms compounds of a deep red colour

with the alkali metals, which on drying become violet and are easily decomposed by carbonic anhydride.

Chrysophanic acid sublimes partly undecomposed. On warming with concentrated nitric acid it is converted into *chrysamminic acid:*

$$C_{14}H_2(NO_2)_4(OH)_2O_2,$$

or tetranitro-chrysophanic acid. The same body is also obtained from aloïn on boiling aloes with concentrated nitric acid and neutralising the evaporated solution with potassic carbonate, the potash salt:

$$C_{14}H_2(NO_2)_4(OK)_2O_2,$$

separating in metallic-looking yellow green plates, which on treatment with dilute acids yields chrysamminic acid in yellow metallic crystals, which dissolve very slightly in water, imparting thereto a fine purple red colour. It behaves like a strongly dibasic acid, and explodes slightly on heating above its fusing point. Reducing agents convert it into *hydro-chrysamide:*

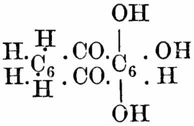
$$C_{14}H_2(NH_2)_3(NO_2)(OH)_2.O_2,$$

beautiful deep blue needles of copper-red lustre, which on carefully heating forms violet vapours like indigo.

1168. *Purpurine, trihydroxy-anthraquinone:*

$$C_{14}H_8O_5 = C_{14}H_5.(OH)_3.O_2,$$

occurs along with alizarine as a decomposition product of the glucosides of madder root, and is also easily produced artificially at the same time as alizarine from substituted anthraquinones. From alizarine and quinazarine it may be obtained by oxidation with MnO_2. From its mode of formation it probably possesses the constitution:



$$\begin{array}{ccccc} & & & \mathrm{OH} & \\ & \mathrm{H} & & | & \\ \mathrm{H.} & \mathrm{C} & \mathrm{.CO.} & \mathrm{C_6} & \mathrm{.OH} \\ \mathrm{H.} & \mathrm{C_6} & \mathrm{.CO.} & & \mathrm{.H} \\ & \mathrm{H} & & | & \\ & & & \mathrm{OH} & \end{array}$$

It forms orange yellow prisms, which may be fused and sublimed without decomposition, are more soluble in water than alizarine, and dissolve in alcohol, ether, and alkalies with a red colour. With lime or baryta water it gives yellow precipitates, and on heating with zinc dust anthracene is obtained.

Purpuroxanthine is the product of the reduction of an alkaline purpurine solution by phosphorus. Hydrochloric acid throws down from this solution yellow flocks of the new body, which may be crystallised from alcohol. It is soluble in acetic acid, benzene, and alkalies, in which latter solution it absorbs atmospheric oxygen, and gives, on the solution being neutralised with an acid, a precipitate of purpurine. This reaction allows purpuroxanthine to be regarded as trihydroxy-dihydranthraquinone, $C_{14}H_5.(OH)_3O_2H_2$.

Among many methods for the preparation of alizarine and purpurine from madder one may be mentioned which makes use of the ready solubility of purpurine in cold solutions of aluminic salts, alizarine being difficultly soluble; another depends on the differing degrees of decomposability of their glucosides. If powdered madder roots are extracted at the ordinary temperature with water containing sulphurous anhydride, and the solution of the glucosides heated to 40°, the purpurine compound only is decomposed with precipitation of purpurine, whilst it is only after the filtrate has been boiled for some hours that alizarine is precipitated in admixture with some other bodies. From this precipitate pure alizarine may be extracted by treatment with hot petroleum of 150°–170° boiling point.

Madder-dyeing depends on the formation of alizarine and purpurine from the glucosides of the root, by fermentation and decomposition with mineral acids. The substance occurring in commerce under the name of *garancine* is powdered madder root that has been treated with sulphuric acid, which therefore contains no ruberythric acid, but only the colouring matters.

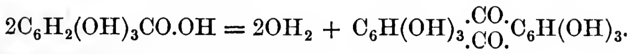
1169. *Tetrahydroxy-anthraquinone*, $C_{14}H_8O_6 = C_{14}H_4(OH_4)O_2$, is known in two isomeric forms, both of which are reduced to anthracene on heating with zinc dust.

1. *Anthrachrysone*, $C_6H_2(OH)_2\genfrac{}{}{0pt}{}{.CO.}{.CO.}C_6H_2(OH)_2$, is obtained from dioxybenzoic acid (§ 1067, 3) by heating with 4 times its weight of sulphuric acid to 140°. It crystallises from alcohol in fine yellow red needles, melting at 320°. It is almost insoluble in water and difficultly so in alcohol and ether. It dissolves in alkaline solutions with a red colour.

2. *Rufiopine*, prepared from opianic acid by heating with sulphuric acid to 180°, crystallises in yellowish red needles and crusts, pretty soluble in alcohol, slightly in boiling water and ether, and gives violet red salts with alkalies.

1170. *Rufigallic acid*, $C_{14}H_8O_3,2H_2O$, is doubtless a hexahydroxy-anthraquinone. It is obtained by heating gallic acid with 4 times its weight of sulphuric acid to 70° or 80°. It forms brown red crystals, which become anhydrous at 120°. It is insoluble in water, nearly so in alcohol and ether. It forms an easily soluble red compound with alkalies and dyes cloth mordanted with alumina a beautiful red.

The formation of rufigallic acid is expressed by the equation :

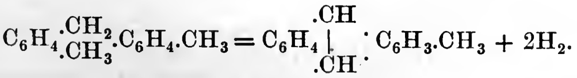


$$2C_6H_2(OH)_3CO.OH = 2OH_2 + C_6H(OH)_3\genfrac{}{}{0pt}{}{.CO.}{.CO.}C_6H(OH)_3.$$

Heating with zinc dust reduces it to anthracene.

Homologues of Anthracene.

1171. *Methyl anthracene*, $C_{15}H_{12}$, is formed on passing the vapour of ditolyl methane (§ 1057, 2) through red-hot tubes filled with pumice, similarly to the formation of anthracene from benzyl toluene :

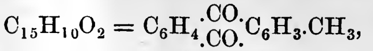


$$C_6H_4\genfrac{}{}{0pt}{}{.CH_2.}{.CH_3}C_6H_4.CH_3 = C_6H_4\genfrac{}{}{0pt}{}{.CH}{.CH}C_6H_3.CH_3 + 2H_2.$$

The sticky mass which collects in the receivers is washed out with alcohol ether, recrystallised from glacial acetic acid, and sublimed, when it forms white yellow or colourless leafy crystals, in the latter case having a strong blue fluorescence, melting between 198° and

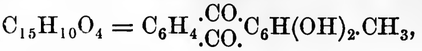
201°. It is only soluble in chloroform, CS_2, and benzol. The picric acid compound forms long red needles.

When an alcoholic solution of methyl anthracene is mixed with strong nitric acid, and afterwards evaporated, a product is obtained which on addition of water yields *methyl anthraquinone*:



$$C_{15}H_{10}O_2 = C_6H_4{\substack{.CO.\\ .CO.}}C_6H_3.CH_3,$$

which crystallises in needles and plates of melting point 162°–163°. Sulphuric acid converts the quinone into sulphonic acids, yielding, on melting with potassic hydrate at 200° and subsequent decomposition of the product with HCl, *methyl alizarine*:



$$C_{15}H_{10}O_4 = C_6H_4{\substack{.CO.\\ .CO.}}C_6H(OH)_2.CH_3,$$

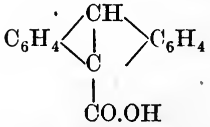
which sublimes between 250° and 252° in red needles and behaves towards alkalies similarly to alizarine.

1172. *Anthracene carbonic acids*, $C_{15}H_9.CO.OH$, isomeric with methyl anthraquinone. On submitting anthracene monosulphonic acids to dry distillation with potassic ferrocyanide, anthracene carbonitrile, $C_{14}H_9.CN$, is produced, which on boiling with alcoholic potash is converted with evolution of ammonia into the potassic salt of *α-anthracene carbonic acid*, which crystallises from hot alcohol in yellow needles, softening between 220° and 230°, but does not decompose even at 280°. It is insoluble in OH_2 and gives easily soluble alkaline salts. The barium and calcium salts are amorphous. The acid yields anthracene on distillation with baric oxide, and on oxidation with CrO_3 gives

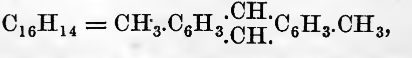
Anthraquinone carbonic acid, $C_{15}H_8O_4 = C_{14}H_7O_2.CO.OH$, which is also produced by oxidising methyl anthracene with chromic acid in glacial acetic acid solution.

It crystallises in yellow needles, melting at 283°, which are sublimable and are very soluble in acetone.

β-Anthracene Carbonic Acid.—On heating anthracene in a sealed tube with $COCl_2$ for some hours to 200° a chloride, $C_{14}H_9.COCl$, is probably produced, the product of the digestion on heating with soda solution and neutralisation with an acid (HCl), giving a precipitate of β-anthracene carbonic acid, which forms yellow silky needles, melting at 206° and splitting up at the same time into CO_2 and anthracene. As this acid is very easily oxidised by chromic acid to CO_2 and anthraquinone, it is probably constituted thus:



1173. *Dimethyl anthracene*:



$$C_{16}H_{14} = CH_3.C_6H_3{\substack{.CH.\\ .CH.}}C_6H_3.CH_3,$$

is formed, analogously to the synthesis of anthracene from benzyl chloride, by heating xylene chloride, $C_6H_4{\substack{.CH_3\\ .CH_2Cl}}$, with water to 180°. It sublimes in white needles having a blue fluorescence.

COMPOUNDS CONTAINING THREE BENZENE NUCLEI.

1174. *Paradiphenyl benzene,* $C_6H_5.C_6H_4.C_6H_5$, is formed along with diphenyl- and isodiphenyl-benzene by passing benzene vapour through a red-hot tube, and alone by treating a mixture of paradibrom-benzene and monobrom-benzene with sodium. It crystallises in flat needles, melts at 205°, and boils at about 400°, dissolves with difficulty in ether and boiling alcohol, easily in benzene. Chromic acid oxidises it to paradiphenyl-carbonic acid (§ 1148), and finally to terephthalic acid.

The isomeric *isodiphenyl-benzene* forms long branching interlaced crystals, fusing at 85° and boiling at about 360°. It yields benzoic acid on oxidation.

1175. The hydrocarbons next to be described are of much greater importance, their derivatives forming to a great extent the colouring matters known as the 'aniline dyes.'

Triphenyl methane, $CH.(C_6H_5)_3$, is the product of the reaction between benzal chloride (§ 1031) and mercury diphenyl at 150° :

$$C_6H_5.CHCl_2 + 2Hg(C_6H_5)_2 = 2Hg(C_6H_5)Cl + C_6H_5.CH:(C_6H_5)_2,$$

and is also formed by heating a solution of diphenyl carbinol (§ 1146) in benzene with phosphoric anhydride :

$$(C_6H_5)_2:CH.OH + C_6H_6 + P_2O_5 = 2HPO_3 + (C_6H_5)_2:CH.C_6H_5.$$

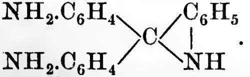
It crystallises from alcohol and ether in shining plates of 92° melting point, and distils above 360°.

Phosphoric chloride converts it into *triphenyl-carbon chloride,* $(C_6H_5)_3:CCl$, which is decomposed immediately by water into triphenyl carbinol; with alcohol it gives the *ethyl ether* of triphenyl carbinol, $(C_6H_5)_3C.O.C_2H_5$ (melting point 78°).

The chloride is decomposed at 200° into HCl and a hydrocarbon, $C_{19}H_{14}$, crystallising in fine needles and melting at 138°, probably *diphenyl-phenylene-methane :*

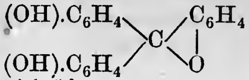
$$(C_6H_5)_2:CCl.C_6H_5 = HCl + (C_6H_5)_2:C:C_6H_4.$$

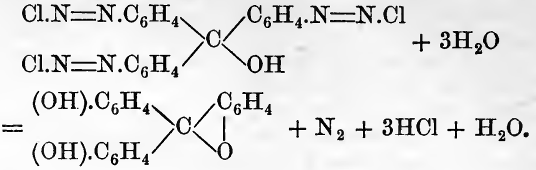
On treatment with nitric acid triphenyl-methane is converted into *trinitro-triphenyl-methane,* $C_{19}H_{13}(NO_2)_3$, a crystalline powder, melting at 207°, and on reduction with zinc yielding *paraleucaniline,* $C_{19}H_{19}N_3$, which on oxidation yields pararosaniline. *Trinitro-triphenyl-carbinol,* $C_{19}H_{12}(NO_2)_3.OH$, is obtained by oxidising trinitro-triphenyl methane with chromic acid; it forms colourless crystals melting at 171°, and by reduction with zinc is converted into *pararosaniline,*



$$\begin{array}{l} NH_2.C_6H_4 \\ \\ NH_2.C_6H_4 \end{array}\!\!>C<\!\!\begin{array}{l} C_6H_5 \\ | \\ NH \end{array}$$

. Pararosaniline can also be prepared from paratoluidine and aniline by the action of oxidising agents. Treated with nitrous acid it yields a diazo compound, whose hydrochloride has the formula $C_{19}H_{13}ON_6Cl_3$, and which on boiling with water yields aurine. On reduction pararosaniline is converted into paraleucaniline, whose diazo compound on boiling with alcohol is converted into triphenyl-methane, thus showing clearly the relations of these substances to that hydrocarbon. In properties paraleucaniline and pararosaniline closely resemble ordinary leucaniline and rosaniline (see later).

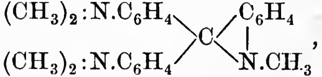
1175*a*. *Aurine*, $C_{19}H_{14}O_3$ =  , is obtained by heating 1 part of oxalic acid with $1\frac{1}{2}$ parts of phenol and 2 parts of sulphuric acid, and, as previously mentioned, by boiling diazo-pararosaniline chloride with water :



It crystallises in shining monoclinic prisms with cantharidine green reflection. Its solutions are of a fine scarlet red. It is insoluble in water, soluble in alkalies, hydrochloric acid, acetic acid, and alcohol; it melts at somewhat above 220°. With alkaline hydric sulphites it yields a colourless crystalline compound :

$$C_{19}H_{14}O_3,KHSO_3,$$

from which aurine is set free by treatment with alkalies or acids, or on boiling with water. On treatment with zinc and acetic acid it is converted into leucaurine, $C_{19}H_{16}O_3$, crystallising from acetic acid in thick prisms. On heating with excess of acetyl chloride it is converted into triacetyl leucaurine, $C_{19}H_{13}(O.C_2H_3O)_3$. This forms short silky needles.

1175*b*. *Methyl aniline violet, Paris violet, pentamethyl pararosaniline*, $C_{24}H_{27}N_3,HCl$ =  ,HCl, is prepared by oxidising dimethyl aniline, best with cupric nitrate, acetic acid, and common salt, at 60°. It forms a lustrous metallic green mass. By treatment with sodic hydrate solution it yields the hydrate $C_{19}H_{13}N_3(CH_3)_5.OH$ as a reddish brown crystalline powder, soluble in alcohol, and also, with fine violet colour, in acids.

1175*c*. *Malachite green, tetramethyl-amido-triphenyl-methane*, $C_{23}H_{26}N_2 = C_6H_5.CH\left\langle\begin{matrix}C_6H_4.N:(CH_3)_2\\C_6H_4.N:(CH_3)_2\end{matrix}\right.$, is formed by heating two molecules of dimethyl aniline and one molecule of benzoic aldehyde with zincic chloride :

$$C_6H_5.CHO + 2C_6H_5.N(CH_3)_2 = C_6H_5.CH\left\langle\begin{matrix}C_6H_4.N(CH_3)_2\\C_6H_4.N(CH_3)_2\end{matrix}\right. + H_2O,$$

and also by heating dimethyl aniline and benzo-trichloride. It is dimorphic, crystallising in plates melting at 93°–94° and in needles melting at 102°.

1176. *Orthotolyl-diphenyl-methane* :

$$C_{20}H_{18} = (C_6H_5)_2C.C_6H_4.CH_3,$$

is obtained by the decomposition of diazo-leucaniline (§ 1180) by boiling alcohol. It forms a crystalline mass, melts at 59·5°, and boils above 360°. Chromic acid in acetic acid solution oxidises it to orthotolyl-diphenyl-carbinol, $C_{20}H_{17}OH$. The hydrocarbon on nitration yields a mixture of nitro products, which on reduction yield leucaniline or rosaniline respectively.

Rosaniline and its Derivatives.

1176*a.* The parent substance from which most of the commercial dyes are formed is *rosaniline*, $C_{20}H_{19}N_3$, a base resulting from one molecule of aniline and two molecules of toluidine, and which can unite with one to three equivalents of acid. The triacid salts, e.g. $C_{20}H_{19}N_3,3HCl$, can only be prepared by the aid of excess of strong acids, and are of a dull yellowish brown colour. Water removes two equivalents of acid from them, leaving the monacid salts. These are nearly insoluble in cold water, but dissolve readily in hot water or alcohol with a fine red colour; their crystals show a beautiful golden green lustre.

Rosaniline can exchange three of the hydrogen atoms united directly to nitrogen for hydrocarbon nuclei (alkyl, &c.), the successive substitution of such atoms changing the colour from the red of the simple salts, through reddish violet, into bluish violet or pure blue. All aniline colours are removed from their solutions by nitrogenous fibres (wool and silk), the latter becoming dyed.

To prepare rosaniline salts, aniline rich in toluidine is heated to 140°–180° either with oxidising agents, such as arsenic acid or mercuric nitrate, or with metallic chlorides which can suffer partial reduction, such as mercuric or stannic chlorides. The formation of rosaniline can be expressed by the equations:

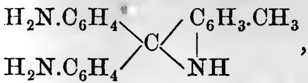
$$C_6H_5.NH_2 + 2C_7H_7NH_2 + 3O = 3H_2O + C_{20}H_{19}N_3$$
$$C_6H_5.NH_2 + 2C_7H_7.NH_2 + 3SnCl_4 = C_{20}H_{19}N_3,HCl + 5HCl + 3SnCl_2.$$

Instead of employing mineral oxidising reagents crude nitro-benzene containing nitro-toluene can be employed, the oxygen of which effects the oxidation of the toluene mixture, whilst the nuclei enter the rosaniline group. The presence of metallic iron and of HCl appears to be essential. The following expresses one of the resulting reactions:

$$C_6H_5.NO_2 + 2C_7H_7.NH_2 = 2H_2O + C_{20}H_{19}N_3.$$

On employment of nitrates as oxidising agents rosaniline nitrate is obtained; metallic chlorides yield rosaniline hydrochloride; arsenic acid gives the arseniate and arsenite. The latter is extracted with water and precipitated as rosaniline hydrochloride by addition of common salt. In every case the salts are repurified by crystallisation.

On heating the aniline colours with concentrated or Nordhausen sulphuric acid the sulphonic acid group ($SO_2.OH$) enters the aromatic nucleus. The resulting monosulphonic acid is in the case of triphenyl rosaniline precipitated by addition of water, converted into the sodic salt, and used under the names of 'Nicholson's' or 'alkali blues' for wool-dyeing. With the disulphonic acids it is necessary to treat the whole melt with milk of lime, and to decompose the lime salts, after filtration, with sodic or ammonic carbonates. These salts then form 'soluble blues,' and are used for dyeing silk or cotton. The sulphonic acids of roseïne, malachite green, and the violets require a similar treatment to that given above for the disulphonic acids of triphenyl rosaniline.

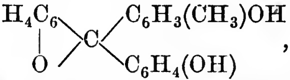
1177. *Rosaniline*,  $(H_2N.C_6H_4)_2C<\overset{C_6H_3.CH_3}{\underset{NH}{|}}$, is obtained as a reddish crystalline precipitate by supersaturating hot aqueous solutions of monacid rosaniline salts, especially the acetate, with ammonia. The quickly filtered solution deposits more of the base on cooling in the form of colourless plates, $C_{20}H_{19}N_3,H_2O$, which are difficultly soluble in water, more readily in alcohol, are insoluble in ether, and are soon coloured red on exposure to air.

Rosaniline hydrochloride, fuchsine, $C_{20}H_{20}N_3Cl$, crystallises in golden green rhombic octahedra, soluble, especially in alcohol, with fine red colour. On heating with strong hydrochloric acid it dissolves with brown colour, forming the triacid salt $C_{20}H_{19}N_3,3HCl$, which separates on cooling in yellowish brown needles.

Rosaniline nitrate, $C_{20}H_{19}N_3.HNO_3$, and *rosaniline acetate:*

$$C_{20}H_{19}N_3.C_2H_4O_2,$$

completely resemble fuchsine, but the latter is decidedly more soluble in water than the two other salts.

1178. *Rosolic acid*, $C_{20}H_{16}O_3=$  $\overset{H_4C_6}{\underset{O}{|}}>C<\begin{matrix}C_6H_3(CH_3)OH\\C_6H_4(OH)\end{matrix}$, homologous with aurine (§ 1175), is prepared by treating rosaniline with nitrous acid and boiling the resulting diazo compound with hydrochloric acid. It forms shining monoclinic prisms, closely resembling those of aurine, and also melting above 220°. With hydric potassic sulphite it gives a crystalline compound, $C_{20}H_{16}O_3,KHSO_3$, from which it can be again separated by boiling with water or addition of acids or alkalies. It unites with nascent hydrogen, forming *leucorosolic acid*, $C_{20}H_{18}O_3$, crystallising in large prisms and yielding with chloracetyl fine needles of the triacetate, $C_{20}H_{15}(O.C_2H_3O)_3$.

1179. *Alkyl-substituted rosanilines* are prepared by heating rosaniline with alkyl iodides and the respective alcohols under pressure at 100°. All three replaceable hydrogen atoms being readily exchanged, trialkyl rosaniline salts, of violet colour in solution, chiefly occur in commerce. The most important is *trimethyl rosaniline hydrochloride:*

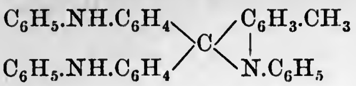
$$C_{20}H_{16}(CH_3)_3N_3,2HCl,$$

known as Hofmann's violet.

On heating rosaniline with aniline, at the boiling point of the latter, and in the presence of a small quantity of an organic acid, acetic or benzoic being generally employed, ammonia is evolved, with formation of mono-, di-, and triphenyl-rosaniline. This introduction of the phenyl groups causes successive alterations of the colours of the solutions, $C_{20}H_{18}(C_6H_5)N_3,HCl$ being red violet,

$$C_{20}H_{17}(C_6H_5)_2N_3,HCl$$

bluish violet, and $C_{20}H_{16}(C_6H_5)_3N_3,HCl$ pure blue. This latter, *triphenyl rosaniline hydrochloride*, forms the dye known as *opal blue*; it is insoluble in water and only slightly soluble in alcohol; on distillation it yields much diphenylamine together with other products. The constitution of *triphenyl rosaniline* is represented by the formula:



1180. A further class of aniline colours consist of trialkyl rosanilines (mostly trimethyl rosanilines) united to methyl haloids, which take the place of the acids.

Iodine green, trimethyl-rosaniline dimethyl-diiodide:

$$C_{20}H_{16}(CH_3)_3N_3,2CH_3I,$$

is prepared from methyl violet by heating with methyl alcohol and methylic iodide, and is formed, together with the violet, by heating rosaniline acetate with double the quantity of methylic iodide and wood spirit in strong closed vessels for ten hours at 100°. After the unaltered liquid ingredients have been distilled off the residue is extracted with a strong solution of common salt, when iodine green goes into solution.

Iodine green crystallises with one molecule of water in cantharidine green prisms; it dissolves in alcohol with a beautiful green colour, which retains its purity in artificial light. The picrate:

$$C_{20}H_{16}(CH_3)_3N_3,2CH_3I,2C_6H_2(NO_2)_3.OH,$$

obtained by addition of picric acid to its solutions, is the salt of iodine green principally met with in commerce.

Trimethyl-rosaniline trimethyl-triiodide:

$$C_{20}H_{16}(CH_3)_3N_3,3CH_3I,$$

can be prepared from the preceding compound.

By the action of ethylic aldehyde on rosaniline dissolved in sulphuric acid, and addition of sodic hyposulphite to the resulting solution after large dilution with water, '*aldehyde green*' is obtained, and can be precipitated from the solution by addition of common salt.

1181. *Leucaniline*, $C_{20}H_{21}N_3$, is the product of the addition of hydrogen to aniline. Its hydrochloride results from the treatment of fuchsine with zinc and hydrochloric acid or with ammonic sulphide. Addition of ammonia to its colourless salts precipitates it as a white difficultly soluble powder, which soon acquires a red colour on exposure to air. Treated with nitrous acid it gives a diazo compound, which, when boiled with alcohol, decomposes into nitrogen and ortho-tolyl-diphenyl methane (§ 1176). The alkyl-substituted rosanilines also unite with two atoms of hydrogen, yielding leuco compounds.

Chrysaniline, $C_{20}H_{17}N_3$, is invariably obtained as a bye product in the manufacture of rosaniline. It is a chrome yellow powder, not very soluble in cold water, readily soluble in alcohol; it dyes silk and wool golden yellow. Like rosaniline it forms stable monacid salts and diacid salts, which are decomposed by water; e.g.

$$C_{20}H_{17}N_3.HNO_3,$$

ruby red needles difficultly soluble, and $C_{20}H_{17}N_3,2HNO_3$, dark red prisms.

Though of other composition, the earliest known aniline colour—*mauveïne*—may be conveniently described here. Its sulphate:

$$C_{27}H_{24}N_4,H_2SO_4,$$

is formed when dilute solutions of a mixture of aniline and toluidine sulphates and potassic dichromate are mixed. The solution is purple red. Addition of alkalies liberates the free base, $C_{27}H_{24}N_4$, as a nearly black crystalline powder, soluble in alcohol with violet colour. All its salts are crystalline and have a cantharidine green lustre. Its formation may be represented by the equation:

$$C_6H_7N + 3C_7H_9N + 5O = C_{27}H_{24}N_4 + 5H_2O.$$

1182. *Paratolyl-diphenyl methane:*

$$C_{20}H_{18} = (C_6H_5)_2CH.C_6H_4.CH_3,$$

results by heating tolyl-diphenyl carbinol with benzene and phosphoric anhydride. It forms colourless crystals, melting at 71° and boiling above 360°.

On oxidation it yields an acid:

$$C_{20}H_{16}O_3 = (C_6H_5)_2:C(OH).C_6H_4.CO.OH,$$

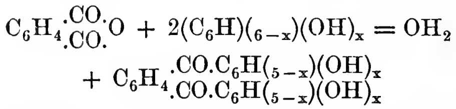
difficult to crystallise, melting at 187°, and giving a barium salt crystallising in silky interlaced needles:

$$(C_{20}H_{16}O_3)_2Ba,7OH_2,$$

difficulty soluble in water.

Phthaleïns.

1183. Phthalic anhydride and phenols, on gently heating with a dehydrating agent, such as sulphuric acid, combine to form the so-called *phthaleïns*, probably according to the equation:

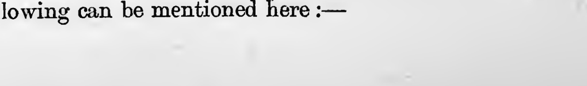


$$C_6H_4\begin{matrix}.CO.\\.CO.\end{matrix}O + 2(C_6H)_{(6-x)}(OH)_x = OH_2 + C_6H_4\begin{matrix}.CO.C_6H_{(5-x)}(OH)_x\\.CO.C_6H_{(5-x)}(OH)_x\end{matrix}$$

They are all soluble in alkalies with formation of brilliant-coloured solutions.

By acting on the bodies in alkaline solution with nascent hydrogen from zinc dust, colourless additions products, phthalines, are obtained, and may be precipitated by acidifying the solutions.

On heating the phthaleïns to a high temperature with sulphuric acid a phenol group in combination with the phthalic acid radical is generally split off in the form of a sulphonic acid, and an anthraquinone derivative is simultaneously produced, thus:



$$C_6H_4\begin{matrix}.CO.C_6H_4.OH\\.CO.C_6H_4.OH\end{matrix} + 2H_2SO_4 = C_6H_4\begin{matrix}.CO.\\.CO.\end{matrix}C_6H_3.OH + C_6H_3(OH)(SO_3H)_2 + 2OH_2,$$

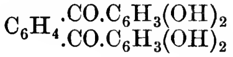
giving a mixture of the two hydroxy-anthraquinones (§ 1167, 2). Resorcin phthaleïn gives alizarine and hydroquinone phthaleïn chinizarine.

Of the numerous compounds already prepared in this group only the following can be mentioned here:—

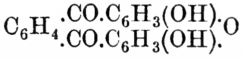
1184. *Phenol phthaleïn*, $C_{20}H_{14}O_4 = C_6H_4(CO.C_6H_4.OH)_2$, isomeric with the phenyl salts of the phenylene dicarbonic acids (§ 1106), is formed by heating five parts of phthalic anhydride with ten parts of phenol and four parts of sulphuric acid at 120°–130°. The red mass, when extracted with water, leaves a resin, which is converted into a clear yellow powder by boiling with benzene. This dissolves in solution of potassic hydrate with fine red colour, without doubt forming $C_6H_4(CO.C_6H_4.OK)_2$, from which addition of hydrochloric acid precipitates phenol phthaleïn as a flocculent mass. The alkaline solution is soon decolourised by contact with powdered zinc, and then yields, on addition of hydrochloric acid, colourless *phenol phthaline*, $C_{20}H_{16}O_4$, whose alkaline solution on exposure to air soon reoxidises and regains its fine colour.

1185. *Resorcin phthaleïn*, or *fluoresceïn*, can be obtained even without the aid of sulphuric acid by fusing two molecules of resorcin with one molecule of phthalic anhydride at 195° until water is no longer evolved. The melt is then boiled with water and the residue, after drying, dissolved in three times its weight of hot acetic acid, the diacetate being formed, which, on addition of alcohol, separates in plates; it is recrystallised from acetone and saponified by boiling with alcoholic potassic hydrate. Addition of acetic acid precipitates the phthaleïn, which can finally be recrystallised from alcohol.

Fluoresceïn exists in two states:



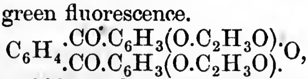
$$\text{as tetrahydrate, } C_{20}H_{14}O_6 = C_6H_4\begin{array}{l}.CO.C_6H_3(OH)_2\\.CO.C_6H_3(OH)_2\end{array}$$



$$\text{and as anhydride dihydrate, } C_{20}H_{12}O_5 = C_6H_4\begin{array}{l}.CO.C_6H_3(OH).\\.CO.C_6H_3(OH).\end{array}O$$

The first is invariably precipitated in yellow flocks, also the latter, from alkaline solutions by supersaturating with acids, and is converted into the anhydride dihydrate by crystallisation from boiling alcohol, by heating alone at 130°, or by heating with sulphuric acid, acetic anhydride, &c. This latter form is obtained first in the synthesis of fluoresceïn; it forms a crystalline brick red powder, nearly insoluble in water, ether, and benzene, difficultly soluble in alcohol and acetone. On dilution of the alcoholic solution it separates in clear yellow stellate needles. It yields alizarine on heating with acids.

It dissolves in solutions of alkalies and ammonia with a beautiful red colour. The ammoniacal solution is characterised by its extraordinarily strong green fluorescence.



The *diacetate*, $C_6H_4\begin{array}{l}.CO.C_6H_3(O.C_2H_3O).\\.CO.C_6H_3(O.C_2H_3O).\end{array}O$, crystallises in colourless plates, melts at 200°, and is not soluble in aqueous alkalies.

Alkaline solutions of fluoresceïn are decolourised by zinc dust; addition of acids then precipitates *resorcin phthaline* or *fluorescine*; oxidising agents reconvert it into fluoresceïn.

Tetrabrom-fluoresceïn, or *eosine*, $C_{20}H_8Br_4O_5$, is readily obtained by the action of bromine on fluoresceïn. It forms a brownish red powder, which crystallises from acetic acid in yellow prisms.

The potassic and baric compounds, $C_{20}H_6Br_4O_5K_2$ and

$$C_{20}H_6Br_4O_5Ba,$$

form red crystals of golden green lustre, dissolving in water and alcohol with a beautiful deep red colour, and on sufficient dilution imparting a greenish yellow fluorescence to the liquid.

1186. *Hydroquinone phthaleïn*, isomeric with the preceding, is obtained by heating phthalic anhydride, hydroquinone, and sulphuric acid. It crystallises from water in colourless nacreous plates:

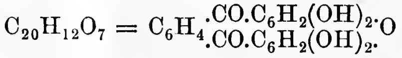
$$C_{20}H_{14}O_6$$

(tetrahydrate), which at 170° is converted into the dihydrate anhydride, $C_{20}H_{12}O_5$, a colourless mass melting at 233°. It dissolves in concentrated sulphuric acid with brick red colouration, in alkalies with a violet colour. Chlor-acetyl converts it into a crystalline diacetate, $C_{20}H_{10}(C_2H_3O)_2O_5$. When strongly heated with sulphuric acid it yields chinizarine.

1187. *Pyrogallol phthaleïn*, or *galeïn*, is obtained directly by heating phthalic anhydride with double its weight of pyrogallol. It dissolves difficultly with red colour in hot water, more readily in alcohol. It can be recrystallised from hot dilute alcohol, and then forms a brownish red mass with blue reflex of the formula:

$$C_{20}H_{14}O_8 = C_6H_4:[CO.C_6H_2(OH)_3]_2,$$

converted at 180° into the anhydride tetrahydrate:



$$C_{20}H_{12}O_7 = C_6H_4\begin{array}{l}.CO.C_6H_2(OH)_2.\\ .CO.C_6H_2(OH)_2.\end{array}O$$

Gallin, or pyrogallol phthaline, $C_{20}H_{18}O_7$, obtained from it by reduction, forms large colourless crystals.

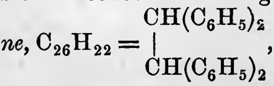
Mellitic and pyromellitic acids yield similar compounds with hydroxy derivatives of benzene.

CONJUGATED COMPOUNDS WITH FOUR BENZENE NUCLEI.

1188. *Triphenyl benzene*, $C_{24}H_{18} = C_6H_3(C_6H_5)_3$(?), is formed by heating phenyl-methyl ketone with phosphoric anhydride or hydrochloric acid gas. It crystallises from absolute alcohol and benzene in short prisms, and melts at 169°–170°.

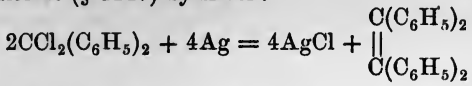
Tetraphenyl methane, $C_{25}H_{20} = C(C_6H_5)_4$, is formed by the action of aluminic chloride on a mixture of carbonic tetrachloride and benzene, also in the dry distillation of baric benzoate. It forms colourless needles, melting at 170°.

Diphenyl-phenylene methane, $C_{25}H_{20} = (C_6H_5.C_6H_4)_2:CH_2$, is obtained by the action of cold sulphuric acid on a solution of diphenyl and methylal in glacial acetic acid (comp. § 1145). It is purified by precipitation with water and solution in benzene, and on evaporation of that solvent forms small colourless monoclinic crystals, melting at 162°. Chromic and sulphuric acids readily oxidise it to *diphenyl-phenylene ketone*, $C_{25}H_{18}O = (C_6H_5.C_6H_4)_2:CO$, which forms granular crystalline aggregates, and readily combines two atoms of nascent hydrogen, forming *diphenyl benzhydrol*, or *diphenyl-phenylene carbinol*, $(C_6H_5.C_6H_4)_2:CH.OH$. This secondary alcohol crystallises in white needles, readily soluble in alcohol and melting at 151°.



Tetraphenyl ethane, $C_{26}H_{22} = \begin{array}{l}CH(C_6H_5)_2\\ |\\ CH(C_6H_5)_2\end{array}$, is obtained by heating benzo-pinacone, hydriodic acid, and phosphorus. It crystallises in prisms, melts at 206°, and can be sublimed.

Tetraphenyl ethylene, $C_{26}H_{20}$, is obtained by dechlorinising diphenyl carbon dichloride (§ 1147) by silver:



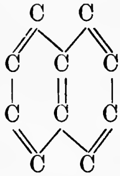
$$2CCl_2(C_6H_5)_2 + 4Ag = 4AgCl + \begin{array}{l} C(C_6H_5)_2 \\ \| \\ C(C_6H_5)_2 \end{array}$$

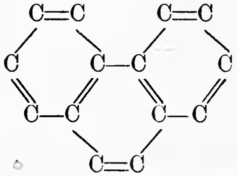
and, together with other hydrocarbons (diphenyl methane, &c.), by heating benzo-phenone and zinc dust. It crystallises from benzene in spear-shaped needles, and is difficultly soluble in alcohol and ether.

Mauveïne probably also belongs to this group.

COMPOUNDS CONTAINING CONDENSED BENZENE NUCLEI.

1189. In these compounds the carbon atoms in the nucleus are arranged in such a manner that the compound is built up of two or more closed hexacarbon chains, a pair of carbon atoms being common to two chains. Assuming the tetravalent nature of carbon, and the correctness of the formula assigned to benzene, no other probability exists than that the carbon atoms common to two rings are *neighbouring* and are in *divalent* union, as shown in the following formula:





These atoms belonging to the two nuclei can evidently not combine with any further elementary atoms (as long as the alternate mono- and divalent union remains), whilst all the others have each one bond available for union with other elementary atoms. If this latter is hydrogen, the hydrocarbons, $C_{10}H_8$,$C_{14}H_{10}$, &c., result. In such hydrocarbons the hydrogen atoms are replaced by other elements or groups according to essentially the same rules as those that regulate substitution in benzene. If the substituting groups are organic radicals, the new compounds formed stand in the same relations to the original molecules that the aromatic compounds containing more than six carbon atoms, previously mentioned, do to benzene.

From their known chemical behaviour *naphthalene* and *phenanthrene* must be included in this group.

NAPHTHALENE AND ITS DERIVATIVES.

Naphthalene, $C_{10}H_8$.

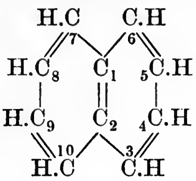
1190. The most important arguments for assigning the more simple nucleus given above to naphthalene are its oxidisability to phthalic acid and the conversion of several of its substitution products into substituted phthalic acids.

From the first it follows that naphthalene must contain at least one orthophenylene nucleus, which remains unchanged in phthalic acid, with which the group C_4H_4 must be united by means of two of its carbon atoms. If in the latter group two atoms of hydrogen are replaced by 2Cl and two others by 2O, *dichlor-naphthoquinone*, $C_6H_4:C_4Cl_2O_2$, results, which on boiling with nitric acid yields phthalic acid, the orthophenylene group remaining intact. By treatment of dichlor-naphthoquinone with phosphoric chloride, pentachlor-naphthalene, $C_6H_3Cl:C_2Cl_4$, is formed according to the equation :

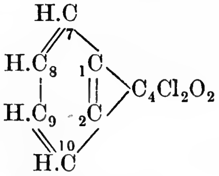
$$C_{10}H_4Cl_2O_2 + 2PCl_5 = 2POCl_3 + HCl + C_{10}H_3Cl_5,$$

and this on oxidation yields not monochlor- but tetrachlor-phthalic acid. For this reaction the formula given above must be rewritten as $C_4H_3Cl:C_6Cl_4$, where C_6Cl_4 is the intact remaining tetrachlor-orthophenylene, and contains the carbon atoms of the groups C_4H_4 and $C_4Cl_2O_2$, which were previously oxidised. Naphthalene must therefore contain *two* orthophenylene groups, which can only be the case on the supposition of two carbon atoms common to both.

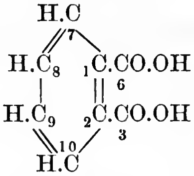
Designating the single carbon atoms in naphthalene by numbers :



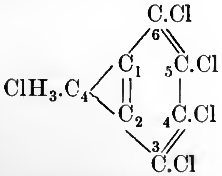
these changes will be represented by the formulæ :



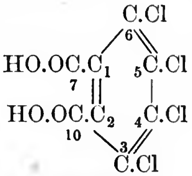
Dichlor-naphthoquinone.



Phthalic acid.



Pentachlor-naphthalene.



Tetrachlor-phthalic acid.

1191. *Naphthalene* occurs to a considerable extent in that portion of coal tar distilling between 180° and 220°, from which it crystallises on cooling. The mass, after freeing from oil by pressing, yields, on recrystallisation from hot alcohol, or more readily by sublimation, pure naphthalene in the form of colourless shining leafy crystals, of peculiar odour and burning taste ; it melts at 79·2° and boils at 218°. Its sp. gr. is ·977 at the fusing point, the vapour density = 4·53. It is insoluble in water, difficultly soluble in cold, readily soluble in hot alcohol, ether, and benzene. On boiling with water it volatilises readily with the aqueous vapour. It burns with a highly luminous, smoky flame, and gives with picric acid a compound:

$$C_{10}H_{18},C_6H_2(NO_2)_3OH,$$

crystallising in fine yellow needles grouped in stellate forms.

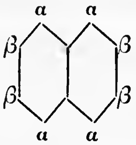
Naphthalene occurs in the products of the dry distillation of nearly all organic bodies, and is obtained by passing the vapour of phenylbutylene dibromide over heated lime:

$$C_6H_5.C_4H_7Br_2 + CaO = CaBr_2 + H_2O + H_2 + C_{10}H_8.$$

On heating with hydriodic acid and amorphous phosphorus at 180° it yields *naphthalene tetrahydride*, $C_{10}H_{12}$, as a colourless liquid lighter than water, which boils at 205° and at a red heat decomposes into naphthalene and hydrogen, and is readily oxidised to phthalic acid by nitric acid.

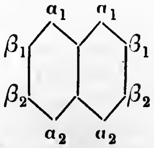
Substitution Products of Naphthalene.

1192. By replacement of a single hydrogen atom in naphthalene two isomeric compounds can result, but in no case have more than two been observed. This agrees with the formula already given, according to which the positions 3, 6, 7, and 10 are of equal value, whilst the positions 4, 5, 8, and 9 are of equal value as regards one another but of different value as regards the first four. These two sets of four positions may be distinguished by the letters α and β as shown in the formula:



With regard to assigning the positions α and β to naphthalene derivatives, it has been shown that on oxidation of ordinary nitronaphthalene, 1:3:4 nitrophthalic acid, melting at 212°, is obtained, from which it follows that the nitro group must have occupied the α position in nitro-naphthalene. By reference to this body the positions of the other naphthalenes can be settled. It may be added that direct experiments have shown that all four α positions are really of the same value in mono-substituted naphthalene derivatives.

In order to indicate the positions to be assigned to the positions of replacement the following signs will be employed:—The numbers 1 and 2 annexed to the α and β positions will serve to show which α or β position is meant. If a single line is drawn between the two symbols, it will indicate that the replacement positions are in the same hexagon, e.g. α_1—β_2; if, on the contrary, two lines are drawn between the symbols, it will indicate that the substitution has occurred in both the hexagons, e.g. α_1=α_1.



On replacement of two hydrogen atoms in naphthalene the possible cases of isomerism become much more numerous. When the replacing groups are the same ten isomers are possible, the number of possible isomers being still larger in the case of the tri (14), tetra (22), and penta (14) derivatives. It is not surprising under these circumstances that considerable uncertainty exists in some of the previous observations and views, and therefore only a few of the more important compounds will be noticed here.

1193. *Chlorine Derivatives of Naphthalene.*—On passing dry chlorine gas into naphthalene, they unite to form *naphthalene dichloride*, $H_{10}H_8Cl_2$, a heavy, pale yellow oil, which unites with more chlorine, being converted into *naphthalene tetrachloride*, $C_{10}H_8Cl_4$. This forms monoclinic crystals and melts at 182°. Continued action of chlorine further converts this into chlorinated chlor-addition products—*chlor-naphthalene tetrachloride*, $C_{10}H_7Cl_5$, melting at 128°–130°, and *dichlor-naphthalene tetrachloride*, $C_{10}H_6Cl_6$, melting at 172°.

These addition products decompose at higher temperatures, or more simply by boiling with alcoholic potassic hydrate, half the added chlorine being eliminated, together with an equal number of hydrogen atoms (comp. § 956), and chlor-substitution derivatives of naphthalene formed.

$C_{10}H_7Cl$, *α-monochlor-naphthalene*, obtained as above from naphthalene dichloride, is a colourless oil; it boils at 263° and again unites with chlorine, forming chlor-naphthalene tetrachloride.

β Monochlor-naphthalene, prepared by the action of phosphoric chloride on β-naphthol, forms colourless crystals, melts at 61°, and boils at 256°–258°.

Dichlor-naphthalenes, $C_{10}H_6Cl_2$. Naphthalene tetrachloride, when boiled with alcoholic potash, gives *α-dichlor-naphthalene* (β—?) as a crystalline mass, melting at 35°–36° and boiling at 280°–282°. Another, *β-dichlor-naphthalene* (α_1—α_2), is obtained by dry distillation of $C_{10}H_8Cl_4$; it melts at 67°–68°, and boils at 281°–283°.

The constitution, source, and melting points of the other dichlor-naphthalenes may be shortly indicated :—

$\alpha_1 = \alpha_2$	from $C_{10}H_7NO_2$ and Cl	m.p. 107°
$\alpha_1 = \alpha_1$	„ β-$C_{10}H_6(NO_2)_2$ and PCl_5	„ 83°
? = ?	„ α-$C_{10}H_6(SO_2OH)_2$ and PCl_5	„ 114°
β = ?α	„ β-$C_{10}H_6(SO_2OH)_2$ and PCl_5	„ 135°
β ?	„ β-$C_{10}H_6(NO_2).SO_2.OH$ and PCl_5	„ 48°
β ?	„ δ-$C_{10}H_6(NO_2)SO_2.OH$ and PCl_5	„ 61·5°

Six *trichlor-naphthalenes*, $C_{10}H_5Cl_3$, have been prepared, of which the most important, *α-trichlor-naphthalene*, prepared from chlor-naphthalene tetrachloride, forms prisms and melts at 81°.

α ? ?	from $C_{10}H_7NO_2$ and Cl	m.p. 90°
α ? ?	„ „ „	„ 103°
$\alpha_1 - \alpha_2 = \alpha_1$	„ PCl_5 and either α- or β-$C_{10}H_5Cl(NO_2)_2$ or γ-$C_{10}H_5Cl_2(NO)_2$	„ 131°
β ? ?	„ η-$C_{10}H_5Cl_2.NO_2$ and PCl_5	„ 65°
β—? = β	„ $C_{10}H_7Cl_4.SO_2Cl$, by successive treatment with alcoholic KHO and PCl_5	„ 56°

Tetrachlor-naphthalenes.—*α-Tetrachlor-naphthalene* ($\alpha_1-\alpha_2$):

$$C_{10}H_4Cl_4,$$

prepared from $C_{10}H_6Cl_6$, crystallises in colourless needles, melting at 130°. Four isomers are known, namely—

?	by the action of chlorine on nitro-naphthalene	m.p. 194°
?	from α-$C_{10}H_6Cl_2Cl_4$ and alcoholic KOH	„ 176°
$\alpha_1=\alpha_2-\beta$	„ α- or γ-$C_{10}H_5Cl_3Cl_2$ or γ-$C_{10}H_6Cl_2Cl_4$, by treatment with alcoholic potash	„ 141°
$\alpha_1=\alpha_2$	„ λ-$C_{10}H_4Cl_2(NO_2)_2$ and PCl_5 . . .	„ 180°

As already mentioned, the action of phosphoric chloride on dichlor-naphthoquinone forms *pentachlor-naphthalene*, $C_{10}H_3Cl_5$, which crystallises in needles and melts at 168·5°. *Perchlor-naphthalene*, $C_{10}Cl_8$ (?), the end product of the action of chlorine on naphthalene, in the presence of antimonic chloride forms prisms melting at 135°.

1194. By bringing together naphthalene and bromine practically only substitution products are obtained. The addition products are far less stable than those of chlorine.

$C_{10}H_7Br$. On mixing solutions of equal molecules of bromine and naphthalene in carbon disulphide, *α-monobrom-naphthalene* is formed as a colourless oil, boiling at 285°. *β-Monobrom-naphthalene* is formed by the action of hydrobromic acid on the diazo compound of β-naphthylamine; it crystallises in white plates and melts at 68°.

α-Dibrom-naphthalene ($\alpha_1-\alpha_2$) is obtained by the further action of bromine on α-monobrom-naphthalene; it crystallises in needles melting at 81°. An isomer melting at 126° ($\alpha_1=\alpha_2$) is obtained, together with another, melting at 77° ($\beta-\beta$), by the decomposition of α-naphthalene sulphonic acid with bromine:

($\beta-$?)	from the action of naphthalene and bromine	melts at	61°
(?=?)	„ α-$C_{10}H_6(SO_2.OH)_2$ and PBr_5	„	140·5°
($\beta=\alpha$)	„ $C_{10}H_6Br_\alpha(SO_2.OH)_\beta$ and PBr_5	„	159·5°
($\alpha_2-\beta_1$)	„ $C_{10}H_5Br_2.NH_2$	„	64°

Tribrom-naphthalenes:

$\alpha_1-\alpha_2=\alpha$	from $C_{10}H_5Br_2(NO_2)$, m.p. 116·5° and PBr_5	m.p. 85°
β ? ?	„ β-$C_{10}H_5Br_2.SO_2.OH$ and PBr_5 . .	„ 86·5°
? ? ?	„ $C_{10}H_6Br_2Br_2$ and alcoholic potash .	„ 75°

Tetrabrom-naphthalene and *pentabrom-naphthalene* are crystalline solids. If naphthalene remains for a long time in contact with excess of bromine it yields colourless rhombic plates of dibrom-naphthalene tetrabromide.

α-Iodo-naphthalene is a colourless liquid, prepared by treating mercury dinaphthyl with iodine; it boils above 300°.

1195. *Nitro-naphthalenes.*—Concentrated nitric acid reacts energetically on naphthalene; in the cold there is formed

α-Nitro-naphthalene, $C_{10}H_7.NO_2$, crystallising in sulphur-yellow prisms, melting at 61° and boiling at 304°. On heating with nitric acid until the oily nitro-naphthalene has disappeared it is converted into two isomeric

Dinitro-naphthalenes, $C_{10}H_6(NO_2)_2$, of which that more difficultly soluble in alcohol ($\alpha_1 = \alpha_2$) forms sublimable colourless prisms, melting at 216°, the more readily soluble *β-dinitro-naphthalene* ($\alpha_1 = \alpha_1$) melting at 170° and exploding at higher temperatures. A third isomer ($\alpha_1 - \beta$), melting at 144°, is obtained by the action of ethylic nitrite on $C_{10}H_5(NO_2)_2NH_2$. Three trinitro-naphthalenes are known: two, melting respectively at 147° ($\alpha_1 = \alpha_2$?) and 122° ($\alpha_1 = \alpha_2$?), are obtained by the action of nitric acid on α-dinitro-naphthalene; the third ($\alpha_1 = \alpha_1$?), melting at 214°, by nitration of β-dinitro-naphthalene. *α-Tetranitro-naphthalene*, $C_{10}H_4(NO_2)_4$, is obtained by nitrating α-$C_{10}H_6(NO_2)_2$; it melts at 259°. *β-Tetranitro-naphthalene* is similarly obtained from β-$C_{10}H_6(NO_2)_2$; it melts at 200°.

1196. *Amido-naphthalenes.*—Unless otherwise mentioned these bodies have been prepared by reduction of the corresponding nitro-naphthalenes by ammonic sulphide or by tin and hydrochloric acid.

α-Amido-naphthalene, naphthylamine, or *naphthalidine*, crystallises in thin colourless prisms, and has an unpleasant odour, like that of the excrements of mice; it is scarcely soluble in water, more readily in alcohol, melts at 50° and boils at about 300°.

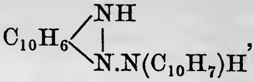
In its chemical behaviour α-amido-naphthalene closely resembles aniline; exposed to air it oxidises, acquiring a red colour. It yields crystalline salts with acids, mostly soluble in water, and on heating with glacial acetic acid forms long fine crystals of *acetnaphthalide*, $C_{10}H_7.N(C_2H_3O)H$, whose solution in glacial acetic acid, on treatment with fuming nitric acid, yields three isomeric *nitro-acetnaphthalides*, $C_{10}H_6(NO_2)N(C_2H_3O)H$. Naphthalidine hydrochloride reacts on aniline on long heating at 280°, forming ammonic chloride and *phenyl naphthalidine*, $C_{10}H_7.N(C_6H_5)H$. This latter crystallises in warty forms, melts at 60°, and possesses very weak basic properties. Treated with carbon disulphide, naphthalidine yields *dinaphthyl thio-urea*, $CS(N.C_{10}H_7.H)_2$.

Nitrous acid converts the salts of α-naphthylamine into those of *diazo-naphthalene*, e.g. $C_{10}H_7.N_2.HNO_3$, which, on boiling their solutions, decompose into nitrogen, free acid, and α-naphthol (comp. § 976). On conducting nitrous anhydride into a cold solution of free naphthalidine, yellowish brown plates of the formula $C_{20}H_{15}O_3$, *diazo-amido-naphthalene*, $C_{10}H_7.N_2.N(C_{10}H_7)H$, separates. It is explosive, and on heating even with weak acids decomposes into nitrogen, α-naphthylamine, and α-naphthol.

β-Amido-naphthalene is obtained by reduction of $C_{10}H_6Br(NO_2)$ (m.p. 131°–132°) with tin and hydrochloric acid; it melts at 112°. Its salts are reduced to those of *β-diazo-naphthalene* on treatment with nitrous acid.

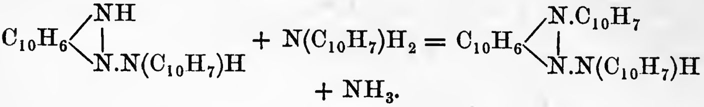
1197. Ammonic sulphide reduces α-dinitro-naphthalene in the cold to *α-nitramido-naphthalene* ($\alpha_1 = \alpha_2$), forming small red crystals melting at 118°–119°, which on further action of reducing agents is transferred into *α-diamido-naphthalene*, or *naphthylene diamine*, $C_{10}H_6(NH_2)_2$ ($\alpha_1 = \alpha_2$). This latter crystallises in shining prisms, melts at 160°, and yields difficultly soluble salts with sulphuric and hydrochloric acids.

Isomeric nitro-amido-naphthalenes have been prepared from nitro-aceto-naphthalidine; one melts at 191° (α_1—α_2), the other at 159° (α_1—β).

Amido-azo naphthalene, $C_{20}H_{15}N_3$ = 

$$C_{10}H_6\left\langle\begin{array}{l}NH\\ |\\ N.N(C_{10}H_7)H\end{array}\right.$$

, isomeric with diazo-amido-naphthalene (comp. § 987), is formed by passing nitrous anhydride into a warm alcoholic naphthalidine solution. It crystallises in orange-red needles of metallic green lustre, melts at 136°, and yields salts with two equivalents of acid. On heating with naphthylamine ammonia is evolved and a new base, *azo-dinaphthylamine*, $C_{30}H_{21}N_3$, formed, whose salts occur in commerce as a fine red dye under the name of Magdala red:



$$C_{10}H_6\left\langle\begin{array}{l}NH\\ |\\ N.N(C_{10}H_7)H\end{array}\right. + N(C_{10}H_7)H_2 = C_{10}H_6\left\langle\begin{array}{l}N.C_{10}H_7\\ |\\ N.N(C_{10}H_7)H\end{array}\right. + NH_3.$$

Tin and hydrochloric acid reduce *amido-azo-naphthalene* to naphthylamine and a second *diamido-naphthalene*, forming shining crystals, which quickly oxidise on exposure to air. A third isomer is obtained by reduction of β-dinitro-naphthalene.

1198. *Naphthalene sulphonic acids* are formed on heating naphthalene with concentrated sulphuric acid. If the temperature is kept as low as possible *α-naphthalene sulphonic acid*, $C_{10}H_7.SO_2.OH$ (m.p. 85°–90°), is principally obtained, together with some quantity of the isomeric *β-naphthalene sulphonic acid.* At 160° only the latter acid is obtained, as the former is converted into it below this temperature. The acids can be separated from one another in the forms of their baric or lead salts, the respective solubilities of which at 10° are—

α-Acid.	
$(C_{10}H_7.SO_2.O)_2Ba,H_2O$	requires 87 parts of OH_2 and 350 parts of 85 % alcohol.
$(C_{10}H_7.SO_2.O)_2Pb,3H_2O$	requires 27 parts of OH_2 and 71 parts of 85 % alcohol.
β-Acid.	
$(C_{10}H_7.SO_2.O)_2Ba,H_2O$	requires 290 parts of OH_2 and 1,950 parts of alcohol.
$(C_{10}H_7.SO_2.O)_2Pb,H_2O$	requires 115 parts of OH_2 and 305 parts of alcohol.

On heating their potassic salts with phosphoric pentachloride isomeric crystalline *naphthalene sulphon-chlorides*, $C_{10}H_7.SO_2Cl$, are formed, of which the α compound melts at 66°, the β compound at 76°. Zinc and dilute sulphuric acid reduce both sulphon-chlorides to *hydrothio-naphthalenes.* The α compound is an oil of nauseous odour, boiling at 285°; the β compound crystallises in scales and melts at 136°; both behave like true mercaptans.

Long-continued heating of naphthalene with much sulphuric acid converts it into two isomeric *naphthalene disulphonic acids.* With sulphuric anhydride naphthalene yields *sulphon-naphthalene*, or *dinaphthyl sulphone*, $(C_{10}H_7)_2SO_2$. Chlorinated, nitrated, amidated, &c., sulphonic and disulphonic acids are known.

Phenol and Quinones of Naphthalene.

1199. *Naphthols*, $C_{10}H_7.OH$. Both the naphthalene hydrates corresponding to the isomeric sulphonic acids are known. They are prepared, analogously to the formation of phenols, from the benzene sulphonic acids, by fusing the respective benzene sulphonic acids with potassic hydrate:

$$C_{10}H_7.SO_2OK + 2KOH = K_2SO_3 + H_2O + C_{10}H_7.OK,$$

and are extracted with ether after the fused mass has been acidulated; they are also obtained by boiling the salts of the corresponding diazo-naphthalenes with water (comp. § 976). They behave towards alkalies, carbonates, &c., like true phenols, and are difficultly soluble in water, even on boiling.

α-*Naphthol* crystallises in monoclinic prisms, melts at 94°, and boils at 278°–280°.

β- or *isonaphthol* forms colourless rhombic tables, melts at 122°, and boils between 285° and 290°.

Ferric chloride oxidises both naphthols to $C_{20}H_{14}O_2$ (naphthyl peroxides, $C_{10}H_7.O.O.C_{10}H_7$?), of which the α compound forms silvery plates, melting at 300°; the β compound crystallises in prisms and melts at 218°.

The potassium derivatives, $C_{10}H_7.OK$, yield with ethylic iodide two isomeric *naphthyl-ethyl ethers*, $C_{10}H_7O.C_2H_5$. The α compound is liquid and boils at 272°; the β-ether is solid, melting at 33°. The naphthols react with acetyl-chloride, forming *naphthyl acetates*:

$$C_{10}H_7.O.C_2H_3O.$$

α-Naphthyl acetate is an oil; the β compound is solid and melts at 60°.

1200. Substitution products of the naphthols have also been prepared. *Nitro-α-naphthols*, $C_{10}H_6(NO_2).OH$. Two bodies of this formula have been obtained by boiling nitro-acetnaphthalides with potash. *α-Nitro-α-naphthol* (α_1—α_2) melts at 164° and crystallises in bright yellow prisms; the isomer (α_2—β) melts at 128° and crystallises in greenish yellow plates. *Nitro-β-naphthol* (β—?) melts at 96°.

Three *nitroso-naphthols* are known, corresponding in composition to the above, into which they are converted by oxidation. They are formed by the action of nitrous acid on the naphthols. The two from α-naphthol melt at 175°–185° and 145°–150° respectively; that from β-naphthol melts at 110°. *Dinitro-α-naphthol* (α_1—β—α_2):

$$C_{10}H_5(NO_2)_2.OH,$$

is of more importance, as its calcic and sodic salts form splendid yellow dyes known as *naphthalene yellow*. It cannot be prepared directly from α-naphthol, but is obtained by the action of nitric acid of 1·35 sp. gr. on naphthylamine, or by heating the latter with diazo-naphthalene hydrochloride. It crystallises from boiling chloro form in shining sulphur yellow needles, melts at 138°, and decomposes carbonates.

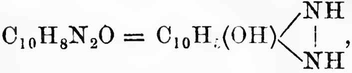
Tin and hydrochloric acid reduce it, large colourless prisms of the double salt of stannous chloride with diamido-naphthol:

$$C_{10}H_5(OH):(NH_3Cl)_2,SnCl_2,2H_2O,$$

being formed. After separation of the tin by sulphuretted hydrogen the solution containing the diamido-naphthol hydrochloride slowly oxidises in the air, or more quickly on addition of ferric chloride, yielding *diimido-naphthol hydrochloride:*

$$C_{10}H_5(OH)(NH_3Cl)_2 + Fe_2Cl_6 + C_{10}H_5(OH)N_2H_3Cl + 2FeCl_2 + 3HCl.$$

From this salt, which crystallises in red prisms or tables of metallic green lustre, ammonia separates yellow crystals of *diimido-naphthol,*



$$C_{10}H_8N_2O = C_{10}H_5(OH)\left\langle\begin{array}{l}NH\\ |\\ NH\end{array}\right.$$

, which appears to be *hydrazo-naphthol* (comp. § 975).

Dinitro-β-naphthol is formed directly on heating β-naphthol with dilute nitric acid. It crystallises in yellow needles, melting at 195°.

1201. *Naphtho-quinone*, $C_{10}H_6O_2$ (α—α), is obtained by oxidation of naphthalene dissolved in glacial acetic acid with chromic acid, the product being then distilled with water. It is readily soluble in ether and hot alcohol, and crystallises in large sulphur yellow tables of persistent odour; it melts at 125°, but sublimes slowly at far lower temperatures. Nitric acid oxidises it to phthalic acid.

β-Naphtho-quinone (β—?) is prepared from nitroso-β-naphthol by amidation followed by oxidation. It crystallises in orange yellow needles and melts at 96°.

Naphtho-hydroquinone, $C_{10}H_6(OH)_2$ (α—α), is prepared by heating naphtho-quinone with hydriodic acid and amorphous phosphorus. It crystallises in needles, is moderately soluble in water, melts at 176°, and is retransformed into naphtho-quinone by oxidising agents.

Dioxy-naphthalene, isomeric with the preceding, is prepared by fusing naphthalene disulphonic acid with potassic hydrate. It crystallises in needles, which become violet-coloured on exposure to light, and melts at 186°. Its alkaline solutions eagerly absorb oxygen and become of a black colour.

A third isomer (α_1=α_2), obtained by indirect processes from

$$C_{10}H_6(NO_2).SO_2OH,$$

prepared from α-naphthalene sulphonic acid, melts above 220°.

1202. *Hydroxy-naphthoquinone,* or naphthalic acid:

$$C_{10}H_5(OH)O_2,$$

is formed by heating diimido-naphthol at 120° with dilute sulphuric or hydrochloric acids:

$$C_6H_5(OH)(NH)_2 + 2H_2O + H_2SO_4 = C_6H_5(OH)O_2 + (NH_4)_2SO_4.$$

It forms clear yellow needles, and can be sublimed; it is but little soluble in boiling water, readily so in alcohol and ether. It decomposes carbonates with evolution of carbonic anhydride, and yields blood red alkali salts, which are readily soluble in water. Tin and hydrochloric acid convert it into

Trihydroxy-naphthalene, $C_{10}H_5(OH)_3$ (α_1—β—α_2), which, after removal of the tin, can be extracted from the solution by shaking with ether. It crystallises in yellow needles, is readily soluble, and, especially in alkaline solutions, exerts a strongly reducing action, potassic naphthalate being formed.

1203. *Dihydroxy-naphthoquinone:*

$$C_{10}H_4(OH)_2O_2\ (\alpha_1—\alpha_2=\alpha_2—?),$$

or *naphthazarine*, is a colouring matter closely resembling alizarine; it crystallises in long red needles of golden green lustre. It is obtained by heating a solution of four parts of α-dinitro-naphthalene in 40 parts of concentrated sulphuric acid and four parts of Nordhausen sulphuric acid to 200°, and then adding fragments of granulated zinc, the temperature being kept between 195° and 205°. As soon as a sample appears of a fine red colour, and separates red flocks on cooling, the solution is diluted with four times its volume of water, filtered from the separated black mass, and the diluted filtrate boiled, whereby the naphthazarine is precipitated. It is obtained pure by recrystallisation from alcohol; it dissolves in alkalies with blue or violet colour.

The following bodies are also disubstituted naphtho-quinones:—

Dichlor-naphthoquinone, $C_{10}H_4Cl_2O_2$ (α_1—β_1—β_2—α_2), is prepared by the action of nitric acid on chlor-naphthalene tetrachloride, or by the oxidation of naphthol or naphthalene yellow with potassic chlorate and hydrochloric acid; it crystallises in golden yellow needles, melts at 189°, and is soluble in alcohol and ether. Hot concentrated nitric acid oxidises it to phthalic acid; phosphoric chloride at 180°–200° converts it into pentachlor-naphthalene (§ 1193), sulphurous or hydriodic acid into *dichlor-dihydroxy-naphthalene:*

$$C_{10}H_4Cl_2(OH)_2,$$

whilst solution of potassic hydrate converts it into the potassic salt of *chlor-hydroxy-naphthoquinone*, $C_{10}H_4Cl(OH)O_2$. This latter is a difficultly soluble, yellow, crystalline powder, which melts above 200° and sublimes in needles. Phosphoric chloride converts it also into pentachlor-naphthalene.

Trihydroxy-naphthoquinone, $C_{10}H_3(OH)_3O_2$, is formed at the same time as naphthazarine as an amorphous powder of red metallic lustre, dissolving in alkalies with bluish violet colour.

1204. *Mercury dinaphthyl*, $Hg(C_{10}H_7)_2$, is prepared by boiling a mixture of brom-naphthalene and benzene with sodium amalgam. It crystallises in rhombic prisms, difficultly soluble in hot alcohol, readily in chloroform; it melts at 243° and generally behaves like mercury diphenyl (§ 980).

Homologues of Naphthalene.

1205. These bodies are prepared by the action of sodium on a mixture of monobrom-naphthalene and an alkyl haloid.

Methyl naphthalene, $C_{11}H_{10} = C_{10}H_7.CH_3$, is obtained as a colourless thick oil of sp. gr. 1·0287, boiling at 232°.

Ethyl naphthalene, $C_{12}H_{12} = C_{10}H_7.C_2H_5$, closely resembles the preceding and boils at 252°.

1206. *Derivatives of Methyl Naphthalene.*—Alcohols:

$$C_{10}H_7.CH_2.OH,$$

have not yet been prepared, but two acids are known of the formula $C_{10}H_7.CO.OH$, the *naphthyl carbonic* or *naphthoic acids* and an aldehyde, $C_{10}H_7.CHO$.

The naphthoic acids are prepared from the potassic naphthalene sulphonates, which by dry distillation with potassic cyanide are each converted into a naphthyl cyanide, $C_{10}H_7.CN$. *α-Naphthyl cyanide* crystallises from alcohol in colourless broad needles, melts at 37·5°, and boils at 298°; *β-naphthyl cyanide* forms plates melting at 66·5° and boiling at 305°. On boiling with alcoholic potassic hydrate both evolve ammonia, and are converted into salts of the corresponding naphthoic acids, from which the free acids can be obtained on acidulating with hydrochloric acid. These closely resemble benzoic acid, form salts, chlorides, amides, ($C_{10}H_7.CO.NH_2$), &c., in the usual way, and yield naphthalene on distillation with lime.

α-Naphthoic acid has also been prepared by fusing α-naphthalene sulphonic acid with sodic formate. It crystallises in colourless needles, melts at 160°, is difficultly soluble in boiling water, readily in hot alcohol. The *calcic salt*, $(C_{10}H_7.CO.O)_2Ca,2H_2O$, requires 93 parts of water at 15° for solution. *Ethylic α-naphthoate* is prepared by the action of sodium amalgam on a mixture of α-brom-naphthalene and ethylic chloro-carbonate (comp. § 1045, 1*a*); it is an oil boiling at 309°. A mixture of fuming nitric acid and sulphuric acid converts α-naphthoic acid into *α-nitro-naphthoic acid*, forming clear yellow needles melting at 194°.

β- or *isonaphthoic acid* melts at 182° and boils above 300°. Its calcic salt requires 1,400–1,800 parts of water for solution. *Nitro-β-naphthoic* acid melts at 228°. On dry distillation of an intimate mixture of calcic β-naphthoate and formate *isonaphthoic aldehyde:*

$$C_{10}H_7.COH,$$

is obtained in the form of leafy crystals, melting at 59·5°; it is scarcely soluble in boiling water, but volatilises in steam.

Phosphoric chloride converts both naphthoic acids into *naphthoyl chlorides*, $C_{10}H_7.COCl$, of which the α compound is liquid at ordinary temperatures, the β-chloride crystalline, but readily fusible.

1207. *Hydroxy-naphthoic acids*, or *carbo-naphtholic acids*:

$$C_{10}H_6(OH)CO.OH,$$

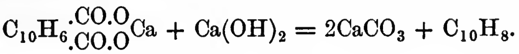
are obtained by the simultaneous action of sodium and carbonic anhydride on the naphthols (comp. salicylic acid, § 1061). *α-Carbo-naphtholic acid* crystallises from alcohol and ether in stellate groups of colourless needles, and melts at 185°–186°; its salts give an intense blue coloration with ferric chloride. *β-Carbo-naphtholic acid* requires further investigation.

Other isomers are obtained by solution of the naphthoic acids in sulphuric acid and decomposition of the resulting *sulpho-naphthoic acids*, $C_{10}H_6\genfrac{}{}{0pt}{}{.SO_2OH}{.CO.OH}$, by fusion with potassic hydrate. The three *hydroxy-a-naphthoic acids* melt respectively at 234°–237°, at 245°–247°, and at 186°–187°; *hydroxy-β-naphthoic acid* melts at 212°–213°.

1207*a*. *Naphthalene dicarbonic acids*, $C_{10}H_6(CO.OH)_2$. Three of these bodies have been prepared by boiling the corresponding *dicyano-naphthalenes* with acids. The source of the cyanides, their melting points, and the melting points of the resulting acids are given below:—

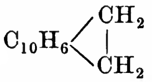
Cyanide.	Resulting Acid.
(α=α) m.p. 204°, from $C_{10}H_6BrSO_2OH$ and KCy .	γ- m.p. 240°.
(?=?) m.p. 262°, from α-$C_{10}H_6(SO_2.OH)_2$ and KCy .	α- m.p. above 300°.
(β—?) m.p. 296°–297°, from β-$C_{10}H_6(SO_2.OH)_2$ and KCy	β- m.p. above 300°.

A fourth isomer, *naphthalic acid*, is obtained by the oxidation of acenaphthene by chromic and dilute sulphuric acids; it crystallises in colourless needles or plates, and decomposes at 140° into water and *naphthalic anhydride*, $C_{12}H_6O_3 = C_{10}H_6\genfrac{}{}{0pt}{}{.CO.}{.CO.}O$, melting at 266°. Calcic naphthalate yields naphthalene on heating with calcic hydrate:

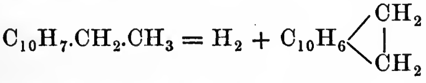


$$C_{10}H_6\genfrac{}{}{0pt}{}{.CO.O}{.CO.O}Ca + Ca(OH)_2 = 2CaCO_3 + C_{10}H_8.$$

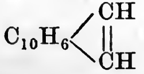
1208. *Acenaphthene*, $C_{12}H_{10}$, probably ethylene naphthalene:



is separated from that fraction of coal tar distilling between 260° and 280°; it can be obtained by passing a mixture of ethylene and benzene vapour through a red-hot tube, or directly from ethyl naphthalene in a similar manner:



$$C_{10}H_7.CH_2.CH_3 = H_2 + C_{10}H_6\genfrac{<}{}{0pt}{}{CH_2}{CH_2}$$

or by heating ethyl naphthalene with a molecule of bromine at 180° and then heating the product with alcoholic potassic hydrate. It crystallises in colourless prisms, melts at 95°, boils at 267°–269°, and is but little soluble in cold alcohol. It unites with picric acid to form red needles of $C_{12}H_{10},C_6H_2(NO_2)_3.OH$. On passing its vapour over ignited plumbic oxide a hydrocarbon, $C_{12}H_8$, melting at 92°, is obtained (acetylene naphthalene =  ?).

1209. *Conjugated Naphthalene Compounds.*—The most important of these bodies are the following:—

1. *Dinaphthyl*, $C_{20}H_{14} = C_{10}H_7.C_{10}H_7$ (α=α), is prepared by

the action of sodium on α-brom-naphthalene, or by partial oxidation of naphthalene with manganic dioxide and sulphuric acid, and by passing naphthalene vapour through a red-hot tube. It crystallises in pearly plates, melts at 154°, can be sublimed, is readily soluble in ether, and yields phthalic acid on oxidation.

Isodinaphthyl (β—β), isomeric with the above, is obtained by passing naphthalene vapour through a red-hot tube; it forms white plates of slight blue fluorescence and melts at 187°. A third isomer (α—β) is obtained at the same time, crystallising in six-sided white plates, apparently monoclinic; it melts at 76°.

2. *Phenyl-naphthyl methane*, $C_6H_5.CH_2.C_{10}H_7$, is obtained by heating 100 parts of benzylic chloride with 80 parts of naphthalene and 15 parts of zinc dust. On distilling the product phenyl-naphthyl methane passes over at 320°–350° as a solid mass, crystallising from alcohol in colourless needles and melting at 64°.

Two *phenyl-naphthyl ketones*, $C_6H_5.CO.C_{10}H_7$, derived from a hydrocarbon of this formula, are formed simultaneously by heating benzoic acid with naphthalene and phosphoric anhydride (comp. § 1147); they are also obtained separately by heating the respective naphthoic acids with benzene and phosphoric anhydride. *Phenyl-α naphthyl ketone* forms prisms melting at 75·5°, the β compound needles melting at 82°. They are decomposed by heated soda lime into benzoate and naphthalene.

3. *Dinaphthyl methane*, $C_{10}H_7.CH_2.C_{10}H_7$, is the chief product of the action of sulphuric acid on a mixture of naphthalene and methylal (comp. § 1145). It crystallises in colourless prisms, melts at 109°, can be distilled unaltered, and yields a compound with two molecules of picric acid, crystallising in reddish yellow prisms and melting at 142°–143°.

Dinaphthyl ketone, $C_{10}H_7.CO.C_{10}H_7$, corresponding to dinaphthyl methane, is known in three isomeric modifications. By heating α-naphthoic acid with naphthalene and phosphoric anhydride at 200°, or α-naphthoyl chloride with zinc and naphthalene, or mercury dinaphthyl with two molecules of isonaphthoyl chloride at 170°, the so-called *α-dinaphthyl ketone* is formed. On heating with soda lime it yields naphthalene, α-naphthoic acid, and *β-naphthoic acid.* From its formation and decomposition it must be the α=β compound.

By heating isonaphthoic acid with naphthalene and phosphoric anhydride, or isonaphthoyl chloride with naphthalene and zinc, two further isomers, β- and *γ-dinaphthyl ketones*, are formed, which are decomposed by heated soda lime into naphthalene and isonaphthoic acid. The differences between the three ketones are shown by their crystalline form, fusion points, and solubility in alcohol at 19°.

α-Dinaphthyl Ketone (α=β).

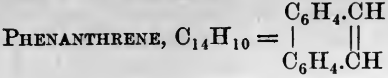
Spear-shaped needles . m.p. 135°. Soluble in 77 parts of alcohol.

β-Dinaphthyl Ketone.

Needles . . . . . . m.p. 125·5°. Soluble in 267 parts of alcohol.

γ-Dinaphthyl Ketone.

Plates . . . . . . m.p. 165°. Soluble in 1,250 parts of alcohol.

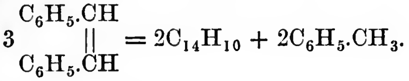


PHENANTHRENE, $C_{14}H_{10} = \begin{array}{l}C_6H_4.CH\\ \mid \qquad \|\\ C_6H_4.CH\end{array}$

1210. Is isomeric with anthracene (§ 1159), and, from its method of formation and reactions, must contain a nucleus of three condensed benzene rings (§ 1189). It occurs in that portion of coal tar boiling between 310° and 350°, and is obtained by recrystallising the pressed solid mass from alcohol. It is obtained in a state of complete purity by decomposition by ammonia of its *picric acid* compound :

$$C_{14}H_{10},C_6H_2(NO_2)_3OH,$$

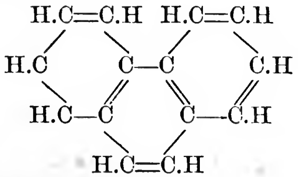
which separates in the crystalline form from a concentrated alcoholic solution. It is formed synthetically, together with toluene, by passing the vapours of stilbene or dibenzyl through a red-hot tube :



$$3\begin{array}{l}C_6H_5.CH\\ \qquad \|\\ C_6H_5.CH\end{array} = 2C_{14}H_{10} + 2C_6H_5.CH_3.$$

It crystallises in colourless plates of blue fluorescence, melts between 96° and 100°, boils at 340°, and dissolves in 50 parts of alcohol at 19°. Chromic and sulphuric acids oxidise it first to phenanthrene quinone, and further to diphenic acid.

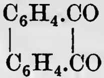
Phenanthrene appears to be a diortho compound, as on oxidation of phenanthrene quinone with alkaline permanganate phthalic acid is obtained. This shows conclusively that the method of union in at least one of the benzene rings is ortho, and renders it highly probable that it is so in both, for it is not likely that if meta or para union occurred no isophthalic or terephthalic acid would be formed, seeing that they are both so much more stable than phthalic acid. Further but more complicated proofs have also been given as to the ortho nature of the union of the two benzene rings, so that the fully detailed formula for phenanthrene becomes :

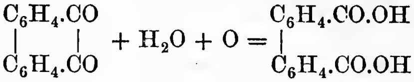


1211. On heating with hydriodic acid and amorphous phosphorus to 210° phenanthrene is converted into *phenanthrene tetrahydride*, $C_{14}H_{14}$, an oil boiling at 300°–310° and difficultly soluble in cold alcohol. Addition of bromine to a solution of phenanthrene in carbon disulphide yields *phenanthrene dibromide*, $C_{14}H_{10}Br_2$, crystallising in colourless prisms and decomposing at 100° into hydrobromic acid and *brom-phenanthrene*, $C_{14}H_9Br$. This latter crystallises in thin colourless prisms, and by further substituting action of bromine yields di- and tri-brom-phenanthrene, $C_{14}H_8Br_2$ and $C_{14}H_7Br_3$.

On heating for a long time with concentrated sulphuric acid phenanthrene yields two sulphonic acids, of which only one has as yet been obtained in the free state.

a-Phenanthrene sulphonic acid forms a crystalline mass; it is readily soluble in water, as are most of its salts.

1212. *Phenanthraquinone,* $C_{14}H_8O_2 =$  $\begin{array}{l} C_6H_4.CO \\ | \qquad | \\ C_6H_4.CO \end{array}$, is formed on mixing hot solutions of 22 parts of chromic acid and 10 parts of phenanthrene in 50 parts of glacial acetic acid; after distilling off the greater part of the solvent it can be separated by addition of water and recrystallised from alcohol. It crystallises in tufts of orange yellow needles, melts at 198°, and can be sublimed without decomposition; it is readily soluble in hot alcohol, in benzene and glacial acetic acid. On gently heating with hydric sodic sulphite it yields a crystalline compound, $C_{14}H_8O_2,NaHSO_3,2H_2O$, which is decomposed by addition of much water. The further action of oxidising agents converts phenanthrene quinone into diphenic acid:

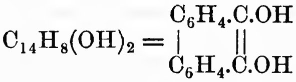


$$\begin{array}{l} C_6H_4.CO \\ | \qquad | \\ C_6H_4.CO \end{array} + H_2O + O = \begin{array}{l} C_6H_4.CO.OH \\ | \\ C_6H_4.CO.OH \end{array}$$

On heating with soda lime it yields diphenyl (§ 1142).

Dibrom-phenanthrene quinone, $C_{14}H_6Br_2O_2$, is obtained by the action of bromine on phenanthrene quinone at 180°; it forms yellow, warty aggregates and melts at 230°. *Dinitro-phenanthrene quinone,* $C_{14}H_6(NO_2)_2O_2$, is obtained by treating phenanthrene quinone with a mixture of sulphuric and fuming nitric acids; it is difficultly soluble in benzene and glacial acetic acid, and melts at 280°.

On warming phenanthrene quinone with aqueous sulphurous acid it forms *phenanthrene hydroquinone:*



$$C_{14}H_8(OH)_2 = \begin{array}{l} C_6H_4.C.OH \\ | \qquad \| \\ C_6H_4.C.OH \end{array}$$

which crystallises in colourless needles, somewhat soluble in hot water, reoxidises to the quinone on exposure to air, and yields with acetic anhydride the diacetate, $C_{14}H_8(O.C_2H_3O)_2$, forming small tables, melting at 202° and soluble in hot benzene.

1212*a*. *Phenanthrol,* $C_{14}H_9(OH)$, is prepared by fusing ammonic a-phenanthrene sulphonate with potassic hydrate. It crystallises in laminæ of bluish fluorescence, melts at 112°, and dissolves readily in alcohol and ether. The *acetate,* $C_{14}H_9(O.C_2H_3O)$, crystallises in shining laminæ and melts at 117°–118°.

1212*b*. *Phenanthrene carbonic acids,* $C_{14}H_9.CO.OH$. Two of these acids have been prepared by distilling the potassic or sodic salts of the phenanthrene sulphonic acids with potassic ferrocyanide, saponifying the resulting nitrils with alcoholic potassic hydrate, and acidifying the solution with hydrochloric acid, when the acids separate in flocks. *a-Phenanthrene carbonic acid* crystallises in colourless curved blades, melts at 266°, and sublimes in fern-shaped leaves with partial decomposition; it is nearly insoluble in water, readily soluble in alcohol, ether, and glacial acetic acid. *β-Phenanthrene carbonic* *acid* crystallises in stellate groups of colourless needles and sublimes in fern-shaped leaves; in solubility it resembles the *a*-acid; it melts at 250°–252°.

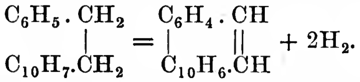
OTHER HYDROCARBONS FROM TAR.

1213. Several other crystalline hydrocarbons have been isolated from the high boiling fractions of coal tar; they belong either to the conjugated or condensed benzene derivatives.

On extraction with carbon disulphide of that part of coal tar distilling at a higher temperature than anthracene *pyrene* goes into solution, whilst *chrysene* remains undissolved.

1. *Pyrene*, $C_{16}H_{10}$. The crude pyrene obtained as above is dissolved in alcohol and precipitated with picric acid, and the crystalline compound so obtained decomposed with ammonia, when pure pyrene is obtained. It crystallises in colourless plates, melts at 142°, and is also readily soluble in ether and benzene. Fuming hydriodic acid at 200° converts it into *pyrene hexahydride*, melting at 127°. Nitric acid and bromine convert pyrene into the respective substitution products; chromic and sulphuric acid oxidise it to *pyrene quinone*, $C_{16}H_8O_2$, which can in part be sublimed unchanged, then forming brick red needles.

2. *Chrysene*, $C_{18}H_{12}$, is obtained by repeated recrystallisation from hot benzene in the form of silver white plates of blue fluorescence; it melts at 250°. It has been prepared synthetically by passing the vapour of the hydrocarbon, $C_6H_5.CH_2.CH_2.C_{10}H_7$ (prepared by reduction of benzyl-naphthyl ketone), through a red-hot tube:



$$\begin{array}{r} C_6H_5\,.\,CH_2 \\ | \\ C_{10}H_7.CH_2 \end{array} = \begin{array}{l} C_6H_4\,.\,CH \\ |\qquad\ \ \| \\ C_{10}H_6.CH \end{array} + 2H_2.$$

With picric acid it yields brown needles of $C_{18}H_2,C_6H_2(NO_2)_3OH$. Nitro and brom substitution products have been obtained, as also, by oxidation with chromic and sulphuric acids, *chryso-quinone*:

$$C_{18}H_{10}O_2.$$

This latter melts at 235° and forms red needles, soluble without decomposition in cold sulphuric acid with blue coloration. It gives a crystalline compound with hydric sodic sulphite. By distillation over heated soda lime it gives a hydrocarbon, $C_{16}H_{12}$; further oxidation converts it into phthalic acid.

3. *Retene*, $C_{18}H_{18}$, is obtained from the tar of coniferæ rich in resin and of beech wood. It forms nacreous plates melting at 98°, boils above 360°, is difficultly soluble in alcohol, readily so in ether and benzene; it yields a red crystalline compound with one molecule of picric acid. Concentrated sulphuric acid dissolves it, forming *retene disulphonic acid*, $C_{18}H_{16}(SO_2.OH)_2$. Chromic and sulphuric acids oxidise it to *dioxy-retistene*, $C_{16}H_{14}O_2$, which crystallises from alcohol in orange yellow needles, melts at 194°–195°, and on heating with zinc dust is converted into the solid hydrocarbon *retistene*, $C_{16}H_{14}$.

ORGANIC SUBSTANCES OF UNKNOWN CONSTITUTION.

1214. Numerous organic substances, many of them well defined, have been prepared from animals and vegetables, but so far there is not enough known of their chemical behaviour, decomposition products, &c., to afford proof of their composition.

By far the largest number of these contain radicals nearly allied to the aromatic compounds, and which indeed often yield well-known benzene derivatives when the decomposition is carried further; they cannot, however, be arranged in a rational system.

In the following pages such *glucosides*, *acids*, *indifferent crystallisable vegetable substances* (colouring matters and bitter principles), *resins*, *alkaloids*, *tannins*, and *proteïds* as are of sufficient importance will be described.

Glucosides.

1215. Under the term glucosides are comprehended ethereal derivatives of the sugars, especially of grape sugar (comp. § 870); they are mostly of natural origin. By the action of dilute mineral acids, and of certain organic substances acting as ferments, they are split up into the sugar, and as a rule only a single other compound.

They are obtained by heating the vegetable matter with hot water or alcohol. The more easily soluble glucosides cannot be thoroughly separated by simple crystallisation from the accompanying substances, such as tannin. In order to remove these latter the solution is treated with neutral plumbic acetate, the lead precipitated from the filtrate by sulphuretted hydrogen, and the filtrate from which the colouring matters have generally been removed by the above processes evaporated to the crystallising point. The constitution of many glucosides is not known, so that formulæ cannot be always assigned to them.

Among the more important glucosides *arbutine*, *salicine*, *populine*, *phloridzine*, *ruberythric acid*, and *franguline* have been described in detail, and amygdaline and myronic acid at least mentioned.

Vegetable Glucosides.

1216. *Amygdaline*, $C_{20}H_{27}NO_{11}$, is the crystallisable bitter principle of bitter almonds. It can be extracted from the meal, which has been pressed as much as possible to remove fat, by means of boiling alcohol. On evaporating the filtrates considerably the amygdaline crystallises out, and is then purified by washing with ether and recrystallising from hot alcohol. Amygdaline is easily soluble in water and hot alcohol.

From the latter it crystallises in pearly scales, from the former in prisms containing three molecules of water of crystallisation. On gently warming with acetic anhydride it forms a *heptacetate :*

$$C_{20}H_{20}(C_2H_3O)_7NO_{11},$$

which crystallises in silky needles from alcohol and ether. Aqueous solutions of amygdaline are decomposed by the ferment emulsin into sugar, hydrocyanic acid, and benzoic aldehyde (§§ 74 and 1031). On long boiling with baryta water ammonia is evolved and the baryta salt of *amygdalic acid*, $C_{20}H_{28}O_{13}$, is formed. The acid is crystalline and deliquescent in moist air. Amygdaline occurs also in the kernels of stone fruit, in the leaves of the cherry laurel (*Prunus Laurocerasus*), and in many other amygdalaceæ and pomaceæ.

1217. *Æsculine*, $C_{15}H_{16}O_9,2H_2O$. Æsculine occurs, together with a little fraxine, in the bark of the horse chestnut (*Aesculus hippocastanum*). If the aqueous extract of the bark be precipitated with plumbic acetate and the excess of lead removed by sulphuretted hydrogen, on evaporating the filtrate æsculine crystallises out mixed with a little fraxine, which latter dissolves first on warming the crystalline magma with water. Æsculine crystallises in colourless needles, which have a faint bitter taste and dissolve difficultly in cold water, easily in hot water and in alcohol.

At about 110° they lose water and at 160° they melt, losing more water. The aqueous solution has a strong blue fluorescence, which disappears on acidifying, but appears again on adding an alkali. Treated with acetic anhydride it yields a hexacetate:

$$C_{15}H_{10}(C_2H_3O)_6O_9,$$

which crystallises in needles and melts at 130°. It is split up by emulsin or dilute acids into sugar and *æsculetine*, $C_9H_6O_4,H_2O$:

$$C_{15}H_{16}O_9 + H_2O = C_6H_{12}O_6 + C_9H_6O_4.$$

Æsculetine occurs ready formed in small quantity in the bark of the horse chestnut. It crystallises with one molecule of water in needles or plates, melts at 270°, and is only soluble with great difficulty in water or alcohol. It is readily soluble, with yellow coloration, in alkalies, and yields with acetic anhydride a *triacetate :*

$$C_9H_3(C_2H_3O)_3O_4;$$

this latter crystallises in silky needles. Hot concentrated solution of potassic hydrate decomposes æsculetine into oxalic, formic, and protocatechuic acids.

Daphnine, isomeric with æsculine, is a glucoside occurring in the bark of many species of daphne (*D. alpina, D. mezereum*). It also crystallises in prisms (with $2OH_2$) and on decomposition yields *daphnetine*, $C_9H_6O_4,H_2O$. This latter loses water at 220° and then sublimes. It yields a monacetyl derivative, $C_9H_5(C_2H_3O)O_4$, m.p. 129°–130°.

1218. *Fraxine*, $C_{27}H_{30}O_{17}$(?), is found together with æsculine in the bark of the horse chestnut, especially in the winter, but occurs in larger quantity in ash bark (*Fraxinus excelsior*), from which it can therefore be most profitably extracted. After precipitating the tannins from the aqueous extract by means of neutral plumbic acetate the fraxine can be thrown down by basic lead acetate and the precipitate suspended in water and decomposed by sulphuretted hydrogen. It crystallises from the filtrate in fine colourless needles grouped in bunches, which only dissolve abundantly in boiling water or alcohol and fuse at a strong heat.

Dilute acids split it up into sugar and *fraxetine :*

$$C_{27}H_{30}O_{17} + 3H_2O = 2C_6H_{12}O_6 + C_{15}H_{12}O_8 \ (?).$$

The *fraxetine* separates out in colourless needles soluble in alcohol. It dissolves in nitric acid, giving first a violet, then red, and lastly yellow colour.

1219. *Quercitrine,* $C_{33}H_{30}O_{17}$. Quercitrine is the glucoside of quercitron, the bark of *Quercus tinctoria.* It occurs also in other plants, such as in sumach, grape vine, and in catechu. The respective substances are extracted with alcohol and the tannin precipitated by means of gelatine solution. On evaporating the filtrate small yellow crystals of quercitrine are obtained, which are but slightly soluble in hot water. Dilute acids split up quercitrine into isodulcite (§ 853) and *quercetine,* $C_{27}H_{18}O_{12}$:

$$C_{33}H_{30}O_{17} + H_2O = C_6H_{14}O_6 + C_{27}H_{18}O_{12}.$$

Quercetine occurs ready formed in other plants, such as tea, bark of the apple tree, &c. Separated from its solutions it forms a yellow crystalline powder, which may be partially sublimed in beautiful yellow needles.

It is readily soluble in alcohol, also in alkalies, with which it forms crystalline compounds. It is coloured green by ferric chloride. Hot and very concentrated alkali solutions decompose it into phloro-glucine (§ 1000) and *quercetic acid,* which crystallises in fine prisms, and by fusing with alkalies is decomposed into various substances, amongst which may be mentioned *paradatiscetine,* $C_{15}H_{10}O_6$, crystallising in fine yellow needles ; *quercimeric acid,* $C_8H_6O_5,H_2O$, which crystallises in thick prisms and gives a fine blue colour with ferric chloride ; and as a final product protocatechuic acid, $C_7H_6O_4$.

The following are very similar to quercitrine :—

Rutine, occurring in *Ruta graveolens* and the flower buds of *Capparis spinosa* (capers) ; it yields quercetine on decomposition.

Datiscine, occurring in the roots of *Datisca cannabina,* which is used in the East as a yellow dye for silk ; it yields sugar and datiscetine on decomposition.

Robinine, from the flowers of *Robinia pseudacacia,* yields quercetine when boiled with dilute acids.

1220. *Convolvuline and Jalapine.*—The roots of jalap (the rhidzomes of *Convolvulus Schiedanus* and *C. orizabensis*) contain as the active principles two amorphous glucosides—in the first *convolvuline,* in the others *jalapine,* which belong to the same homologous series, since their compositions not only differ by C_3H_6 but also yield homologous products on decomposition. In order to prepare them the jalap roots must be several times extracted with water, and then with alcohol, the colour removed by animal charcoal, and the filtrate evaporated down on the water bath. The residue is then treated with alcohol and the glucosides precipitated by ether.

Convolvuline, $C_{31}H_{50}O_{16}$, and *jalapine*, $C_{34}H_{56}O_{16}$, are amorphous, colourless and odourless masses, slightly soluble in water, very easily soluble in alcohol and in dilute acids, not at all in ether; they act as purgatives. On heating they fuse (convolvuline fuses at 150°), and are decomposed at a rather higher temperature. They are dissolved by strong bases, forming the salts of the easily soluble acids *convolvulic acid*, $C_{31}H_{52}O_{17}$, and *jalapic acid*, $C_{34}H_{58}O_{17}$. These acids are most easily prepared by boiling the original glucosides with baryta water, and, after accurately precipitating the barium with sulphuric acid, evaporating the filtrate, when they are obtained as easily soluble, amorphous bodies, melting a little above 100°. The salts, whether containing one or two equivalents of metal, are also amorphous.

The original bodies or the acids are decomposed by emulsin, yielding sugar. Convolvuline gives at the same time *convolvulinol*:

$$2C_{13}H_{24}O_3,H_2O,$$

jalapine similarly yielding *jalapinol*, $2C_{16}H_{30}O_3,H_2O$:

$$C_{31}H_{50}O_{16} + 5OH_2 = C_{13}H_{24}O_3 + 3C_6H_{12}O_6.$$

Both crystallise in indistinct cauliflower-like masses, are insoluble in water, soluble in alkalies, giving salts of *convolvulinolic acid*, $C_{13}H_{26}O_4$, and *jalapinolic acid*, $C_{16}H_{32}O_4$. These acids are difficultly soluble in water, and are therefore precipitated on acidifying solutions of the salts. They both form fine crystalline masses, feeling fatty when touched; the salts are crystalline. Convolvulinolic acid melts at 40°–50°, jalapinolic acid at 64°. Nitric acid oxidises them to *ipomic acid*, isomeric with sebacic acid.

Jalapine occurs also in scammony resin, the hardened juice of *Convolvulus Scammonia*. An isomeric body, *turpethine*, is found in turpeth resin (from the roots of *Ipomoea Turpethum*); it yields amorphous *turpethic acid*, $C_{34}H_{60}O_{18}$, when treated with baryta water, and is decomposed on boiling with dilute acids into sugar and amorphous *turpetholic acid*, $C_{16}H_{32}O_4$.

Convolvulinolic, jalapinolic, and turpetholic acids, having the general formula $C_nH_{2n}O_4$, are apparently homologues of glyceric acid; at all events they do not belong to the aromatic series.

1221. *Saponine*, $C_{32}H_{54}O_{18}$ (?), is found in many plants—for instance, in the kinds of lychnis (*Lychnis Gythago*), in the roots of *Polygala senega*, &c., but especially in the roots of *Saponaria officinalis*.

By boiling the latter with alcohol and cooling the hot filtrate it is obtained in colourless amorphous masses. It is rather soluble in water, forming a solution which behaves like soap solution when shaken; it is only slightly soluble in cold alcohol, not at all in ether. It is poisonous and its dust causes violent sneezing. It is split up by strong HCl into an uncrystallisable sugar and *sapogenine*, $C_{14}H_{22}O_4$. The latter forms white, difficultly soluble crystals.

1222. *Chinovine*, $C_{30}H_{48}O_8$, is a constituent of many cinchona barks, especially of *China nova* and of tormentil roots. From the former it may be prepared by extracting repeatedly with water, treating with milk of lime, and precipitating the filtered solution with hydrochloric acid. The precipitate must be redissolved in alcohol and reprecipitated by water. It is white, amorphous, easily powdered, and tastes intensely bitter. On heating with hydrochloric acid and alcohol it is split up into a sugar like mannitan and *chinovic acid*, $C_{24}H_{38}O_4$, which separates as a shining crystalline powder difficultly soluble even in boiling alcohol. With alkalies and ammonia it yields easily soluble salts, from which the voluminous white silver salt, $C_{24}H_{36}Ag_2O_4$, may be precipitated.

1223. *Glycyrrhizine*, $C_{24}H_{36}O_9$, occurs in liquorice root (*Glycyrrhiza glabra*), from which it may be extracted by boiling water. It is then precipitated by plumbic acetate and the precipitate suspended in water, decomposed by sulphuretted hydrogen. On evaporation of the solution the glycyrrhizine is left as a light yellow amorphous powder, which at first tastes sweet and afterwards has an irritating effect. Boiling dilute acids decompose it into a sugar and *glycyrrhetine*, $C_{18}H_{26}O_4$.

1224. *Helleboreïne*, $C_{26}H_{14}O_{15}$, is obtained from the roots of *Helleborus niger*, and also from *H. viridis*, but in smaller quantity, in the form of microscopic colourless needles, readily soluble in water, difficultly in alcohol. On boiling with dilute acids it yields sugar and *helleboretine*, $C_{14}H_{20}O_3$, which is at first violet blue, but becomes greyish green after drying.

Helleborine, a substance crystallising in colourless concentrically grouped needles, also occurs in quantity in *Helleborus viridis*, but only sparingly in *H. niger*. It is insoluble in water, readily soluble in alcohol, and is coloured intensely red by strong sulphuric acid. Boiling dilute acids convert it into sugar and amorphous *helleboresine*, $C_{30}H_{38}O_4$. Both glucosides act as narcotics, especially helleborine.

1225. *Digitaline* is the bitter, highly poisonous constituent of *Digitalis purpurea*. It is almost insoluble in water, readily soluble in alcohol and chloroform. On heating with concentrated phosphoric and hydrochloric acids it gives an intense green colour; boiling dilute sulphuric acid converts it into sugar and resinous *digitalretine*.

Antiarine, $C_{14}H_{20}O_5$, is extracted by alcohol from the Indian arrow poison, *Upas antiar*, the dried milky juice of *Antiaris toxicaria*, and is obtained on evaporation in colourless crystalline leaves, melting at 220°; the melted mass becomes amorphous on cooling. Antiarine is soluble both in water and ether, and when introduced into a wound it acts as a violent poison. It is split up by dilute mineral acids into sugar and a resinous body.

1226. *Carminic acid*, $C_{17}H_{18}O_{10}$, is found in many plants—for instance, in the blossoms of *Monarda didyma*—but especially in *cochineal*, the female of *Coccus cacti*. The pulverised insects must be extracted with boiling water, the filtrate treated with plumbic acetate, and the washed precipitate suspended in water and decomposed by hydric sulphide. The filtered solution, when evaporated, leaves the acid as a purple red amorphous mass, which yields with bases salts of the same colour. By boiling with dilute acid it yields an optically inactive sugar, which is amorphous and not capable of fermentation, and the dark purple *carmine red*, $C_{11}H_{12}O_7$, soluble in water and alcohol. Carmine red heated with strong nitric acid yields *oxalic acid* and *nitrococcic acid*, $C_8H_5(NO_2)_3O_3$, crystallising in yellow tables, probably a *trinitro-cresotic acid* (§ 1080). Similar valuable red colouring matters occur in other varieties of coccus, such as *C. ilicis* and *C. lacca.*

1227. *Pinipicrine,* $C_{22}H_{36}O_{11}$, is found in the bark and leaves of *Pinus sylvestris,* also in the green parts of *Thuja occidentalis.* It is a yellow amorphous bitter, and yields sugar and ericinol as decomposition products.

Ericoline, $C_{34}H_{56}O_{21}$, occurring in *Ledum pallustre, Erica herbacea,* &c., is a bitter powder which also splits up into sugar and ericinol.

Ericinol, $C_{10}H_{16}O$, is a colourless oil which rapidly darkens in air.

1228. *Caincine,* from the roots of *Chiocca racemosa,* crystallises in difficultly soluble prisms. Hydrochloric acid gas decomposes it into an amorphous sugar and *caincetine,* $C_{22}H_{34}O_3$, and fusion with potassic hydrate converts the latter into butyric acid and *cainceginine:*

$$C_{14}H_{24}O_2.$$

Amongst the other numerous vegetable glucosides it is only necessary to mention the amorphous, insoluble *apiine,* from *Apium petroselinum; crocine,* from saffron; *cyclamine,* from the bulbs *Cyclamen europaeum; ononine,* from the roots of *Ononis spinosa.*

1229. *Myronic acid,* occurring as potassic salt in the seeds of the black mustard, occupies a peculiar place amongst the glucosides. Ground mustard, when treated with boiling alcohol and afterwards with cold water, yields to the latter potassic myronate:

$$C_{10}H_{18}NKS_2O_{10}.$$

The filtered liquid, after evaporation to a syrup, yields a precipitate of the salt on addition of 85 % alcohol. It crystallises in silky needles, and is quickly converted by myrosine, a ferment contained in mustard seeds, into grape sugar, oil of mustard, and hydric potassic sulphate:

$$C_{10}H_{18}NKS_2O_{10} = C_6H_{12}O_6 + C_3H_5NCS + KHSO_4.$$

The aqueous solution of the salt, treated with argentic nitrate, yields a curdy precipitate of $C_4H_5NAgS_2O_4$, sugar remaining in solution. By decomposing this precipitate, suspended in water, by sulphuretted hydrogen, there are formed argentic sulphide, sulphuric acid, free sulphur, and allylic cyanide:

$$C_4H_5NAg_2S_2O_4 + H_2S = Ag_2S + H_2SO_4 + C_3H_5.CN + S.$$

Myronic acid is not known in the free state, as it decomposes so very quickly.

Tannins.

1230. Probably the greater number of the so-called *tannins* belong to the vegetable glucosides; indeed, it is highly probable that tannic acid, from galls, exists in them, to some extent at all events, in the form of a glucoside.

All tannins show the following characteristic properties:—They have an astringent taste, they give a bluish or greenish black precipitate with ferric salts, and are precipitated by gelatine solutions and animal membranes, especially the skin, forming *leather.* Tannins exist in most plants, but in very variable quantities. On boiling with dilute acids many of them yield sugar and red amorphous substances which are insoluble in water, but soluble in alkalies and in alcohol.

These red bodies are also found ready formed in the plants, and are probably the cause of the red brown colour of the bark. In order to obtain tannin the vegetable substances must be extracted with water, the filtered solution precipitated with neutral or basic lead acetate, and the precipitate decomposed under water. On evaporation of the clear liquid the tannin will be left as an amorphous gummy mass.

All tannins yield aromatic compounds when their decomposition products are fused with potash; most of them give phloroglucin and protocatechuic acid.

Oak-bark tannin gives a blue-black colour with ferric salts; on boiling with acids it yields a sugar and phlobaphene (*oak red*):

$$C_{14}H_{10}O_6,H_2O.$$

Cinchona-bark tannin exists combined with the cinchona alkaloids, and on boiling with dilute acids gives *quina red.*

The tannins from *ratany, fern roots,* and *septfoil* all yield red decomposition products, which give phlorogulcin and protocatechuic acid when fused with potash.

Pomegranate tannin yields ellagic acid and sugar.

The tannin of *coffee* has been already described (§ 1100).

Kino tannin, from *kino,* the dried sap of *Pterocarpus erinaceus,* &c., and *catechu tannin,* from *catechu,* the dry extract of *Acacia Catechu, Areca C.,* and *Nauclea Gambir,* may be extracted from the drugs mentioned by means of cold water. They give with ferric salts a dirty green colour, and on melting with potash yield protocatechuic acid and afterwards pyrocatechin.

Maclurin (§ 1236) is also nearly allied to the tannins.

Animal Glucosides.

1231. *Chitine,* $C_9H_{15}NO$, is the basis of the protective coverings of the articulata, and is found in large quantities in the shells of the crustaceæ and the wing cases of beetles. As it is entirely insoluble in water, alcohol, dilute acids, and alkalies, even at the boiling point, it may be obtained pure by boiling crabs or beetles with these liquids and finally washing the residue with pure water. So obtained it forms a colourless, generally translucent mass, having the form of the original material, and chars on heating without previous fusion.

Chitine dissolves in cold concentrated sulphuric acid. The solution, on dilution with water, yields much grape sugar together with nitrogenous decomposition products, especially ammonia.

Hyaline occurs in echinococcus, and is obtained therefrom in a similar manner to chitine, except that in the case of hyaline the acids and alkalies must be used cold. Treated with water at 150° it forms a clear solution. On boiling with dilute sulphuric acid it yields nitrogenous decomposition products and about 50 per cent. of dextrose.

1232. *Cerebrine* is a constituent of the brain, nervous substance, and of the pus corpuscles. It is best obtained from brain; this is rubbed down to a paste, mixed with much alcohol, and allowed to stand for a considerable time. After pressing the residue is washed repeatedly with ether to remove lecithin and cholesterin, and finally extracted with boiling alcohol. On cooling cerebrine mixed with a little lecithin separates out. In order to decompose the latter the mixture must be boiled with baryta water, and after passing a current of carbonic anhydride the precipitate collected, washed with cold alcohol, and lastly extracted with boiling alcohol. Cerebrine separates out from the hot filtrate as a light white hygroscopic powder, which softens at 80°, at the same time becoming brown. It swells up in water and forms a pasty mass. It is split up easily by dilute acids, yielding a lævorotatory unfermentable sugar and other products.

Chondrin also seems to be a glucoside.

ACIDS.

1233. Several of the acids occurring in lichens have been already described.

Usnic acid, $C_{18}H_{18}O_7$, is found in all members of the species *Usnea* and in many other lichens, and is obtained from them like the above-mentioned acids. It crystallises in yellow leaves or prisms, which are insoluble in water and only difficultly soluble in alcohol and ether. Its melting point is about 202° (beta-usnic acid, from *Cladonia rangiferina*, melts at 175°). It is easily soluble in alkalies, but the solutions soon take up oxygen from the air and become brown. On dry distillation it yields *beta-orcin*, $C_8H_{10}O_2$, a substance isomeric with hydrophlorone (§ 1018). This beta-orcin forms easily soluble quadratic prisms, which may be sublimed, and it has the properties of a diatomic phenol.

Vulpic acid, $C_{19}H_{14}O_5$, may be obtained from the lichen *Cetraria vulpina* by treatment with warm lime-water. On acidifying the filtrate it is precipitated in yellow crystals. When crystallised from chloroform thick prismatic crystals are obtained. With the alkalies and alkaline earths the acid forms monobasic, yellow, soluble salts; the salts of the other metals are generally insoluble. It melts at 110°. On boiling with baryta water it yields phenyl-acetic acid (§ 1072), oxalic acid, and methyl alcohol; but if dilute potash be employed the products are methylic alcohol, carbonic anhydride, and *oxaltoluic acid*, crystallising in colourless prisms which melt at 154°. The latter is split up into oxalic acid and toluene by concentrated potash.

Cetraric acid, $C_{18}H_{16}O_8$, and *lichenstearic acid*, $C_{14}H_{24}O_3$, occur in Iceland moss (*Cetraria islandica*). The former crystallises in needles having a bitter taste, the latter in leaflets. Both are insoluble in water.

1234. *Veratric acid*, dimethyl-protocatechuic acid:

$$C_9H_{10}O_4 = C_6H_3(OCH_3)_2CO.OH,$$

(comp. § 1067, 2), isomeric with evernic and umbellic acids (§ 1087), is nearly allied to the lichen acids. It exists in sabadilla seeds. On extracting the seeds with alcohol containing sulphuric acid it dissolves out together with veratrine sulphate (vide alkaloids). After precipitating the sulphuric acid with milk of lime the liquid is filtered and the alcohol distilled off. Veratrine separates out and the calcium salt of veratric acid remains in solution. The acid is precipitated by hydrochloric acid and crystallised from alcohol. It forms colourless prisms, which are difficultly soluble in water, and is decomposed by gently warming with baryta into barium carbonate and *veratrol*, $C_8H_{10}O_2$, a substance isomeric with hydrophlorone and beta-orcin, which melts at 15° and boils at 205°.

Ferulic acid, $C_{10}H_{10}O_4$, may be precipitated as lead salt from the alcoholic extract of assafœtida, and obtained in the free state by treating the precipitate with alcohol containing sulphuric acid. It crystallises in long colourless needles, melting at 154°, and is almost insoluble in water. It is decomposed by potash into acetic and protocatechuic acids.

Sinapic, hemipinic, opianic, and piperic acids will be described under the alkaloids, of which they are decomposition products.

INDIFFERENT CRYSTALLISABLE VEGETABLE SUBSTANCES.

1235. Many bodies free from nitrogen are classed in this group, of which the constitution is at present unknown. Many of them yield metallic compounds with strong bases, without, however, possessing definite acid properties. As many of them may be transformed into phenol-like bodies it is possible that the production of these metallic compounds depends on the presence of a hydroxyl group situated as in phenol.

1236. 1. *Morine*, $C_{12}H_{10}O_6$, occurs mixed with maclurine in fustic, the wood of *Morus* or *Maclaura tinctoria*. The boiling aqueous extract deposits morin on cooling, but the maclurin can only be obtained by evaporating the liquid. They may be purified by recrystallisation after the addition of a little hydrochloric acid to remove calcium.

Morine crystallises in yellow needles, easily soluble in alkalies, ammonia, and alcohol, difficultly soluble in water. The alcoholic solution gives a green colour with ferric chloride. The ammoniacal solutions yield yellow precipitates with calcium chloride and lead acetate. Morine reduces argentic nitrate at ordinary temperatures.

Sodium amalgam and water converts morin into phloroglucin. Fusing with potash gives the same result.

2. *Maclurine*, $C_{13}H_{10}O_6$, forms an almost colourless crystalline powder. It gives a dark green precipitate with ferric chloride. Melted with potash it yields phloroglucin and protocatechuic acid, and gives pyrocatechin on dry distillation. It is therefore probably an ethereal compound of the two first

$$C_6H_3(OH)_2.O.C_6H_3(OH).CO.OH.$$

1237. *Catechine*, *luteoline*, and *scoparine* yield the same products as maclurine on fusion with potash and on dry distillation.

1. *Catechine*, $C_{19}H_{18}O_8$ (?). That portion of catechu and kino insoluble in cold water is extracted with boiling water. On cooling the solution it crystallises out in colourless silky needles, containing water of crystallisation, which after drying at 100° melt at 217°.

2. *Luteoline*, $C_{20}H_{14}O_8$, contained in weld (*Reseda luteola*), forms

fine yellow needles, which melt above 320° and sublime partially undecomposed. It is only slightly soluble in water, more easily, however, in alcohol and in alkalies, to which latter it gives a deep yellow colour.

3. *Scoparine*, $C_{21}H_{22}O_{10}$, exists in *Spartium scoparium* together with the alkaloid sparteïne. It is difficultly soluble in cold water, easily, with yellow colour, in alkalies.

1238. *Athamantine*, $C_{24}H_{30}O_7$, is extracted from the roots and seeds of *Athamantha Oreoselinum* by means of ether, and remains after evaporation of the solvent as an oil which rapidly crystallises. It crystallises in four-sided needles or prisms, melting at 79°, and is insoluble in water. It yields crystalline compounds with hydrochloric acid and sulphurous anhydride. The former decomposes on boiling with water into free hydrochloric acid, and valerianic acid, and *oreoselon:*

$$C_{24}H_{30}O_7 = 2C_5H_{10}O_2 + C_{14}H_{10}O_3 \text{ (oreoselon).}$$

Oreoselon crystallises in colourless needles, difficultly soluble both in alcohol and ether. On boiling it yields *oreoselin*, a substance easily soluble in water, alcohol, and ether:

$$C_{14}H_{10}O_3 + H_2O = C_{14}H_{12}O_4.$$

1239. *Peucedanine*, $C_{16}H_{16}O_4$, is extracted from the roots of *Peucedanum officinale* and *Imperatoria ostruthium* by means of alcohol, and crystallises in small six-sided prisms, melting at 81°–82°. Heated with hydrochloric acid it yields a gas burning with a greenish flame (probably methyl chloride) and *oroselon*, $C_{14}H_{12}O_4$, melting at 177°. Peucedanine is therefore dimethyl oroselon. Oroselon is decomposed by melting potash into acetic acid and resorcin.

Ostruthine, $C_{14}H_{17}O_2$, occurs with peucedanine in imperatoria root. It crystallises from alcohol or ether in rhombic prisms, melting at 115°. Its dilute alcoholic solutions possess a sky-blue fluorescence.

1240. *Santonine*, $C_{15}H_{18}O_3$, is the active constituent of the blossoms of *Artemisia Santonica*. It is obtained by mixing the substance with half its weight of quick-lime and extracting the mixture with dilute alcohol. The filtrate is evaporated and the residue boiled with acetic acid. On cooling santonine crystallises out in lustrous six-sided flat prisms, which melt at 168°-170° and possess a slight bitter taste. It becomes yellow on exposure to daylight. It is quite insoluble in cold water, easily soluble in alcohol and in ether. Heated in a stream of hydrogen with zinc dust it yields *santonol*, $C_{15}H_{18}O$, crystallising in colourless needles which melt at 135°.

Santonine dissolves in alkalies, yielding salts of *santonic acid*. The sodium salt is $2C_{15}H_{19}NaO_4,6H_2O$. These salts, when treated with hydrochloric acid and shaken with ether, yield santonic acid to the latter. It crystallises in difficultly soluble, colourless needles. At 120° it splits up into water and santonine.

The insoluble barium salt dissolves on prolonged boiling with baryta water. On acidifying and extracting with ether an acid is obtained isomeric with the one just described. It melts at 161°–163° without decomposition, and cannot be reconverted into santonine.

Kosine, $C_{31}H_{38}O_{10}$, the active principle of the kousso plant, crystallises in yellow needles or prisms, melting at 142°, insoluble in water, but readily soluble in ether, chloroform, benzol, or boiling alcohol. It yields a hexacetate, melting at 135°, when heated to 150° with acetic anhydride :

$$C_{31}H_{32}(C_2H_3O)_6O_{10}.$$

1241. *Aloine*, $C_{17}H_{18}O_7$, is obtained from the dried sap of the various kinds of aloe by treatment with water and evaporation of the solution in vacuo. It forms small colourless crystals, having a taste both bitter and sweet. It dissolves with difficulty both in alcohol and water, and on warming becomes brown and amorphous. It does not appear to possess purgative properties. On boiling aloes with dilute sulphuric acid paracoumaric acid (§ 1099, 2) is obtained. Aloes treated with nitric acid yield, first, amorphous *aloëtic acid :*

$$C_{14}H_4(NO_2)_4O_2,$$

which is converted by the further action of the acid into chrysammic acid, $C_{14}H_2(OH_2)(NO_2)_4O_2$ (§ 1167, 5). Fused with potash aloes yield *alorcic acid :*

$$C_9H_{10}O_3,H_2O$$

(which crystallises in needles melting at 115°), and eventually acetic, paraoxybenzoic, and oxalic acids.

1242. *Braziline*, $C_{22}H_{18}O_7$, is the colouring matter obtained from Brazil wood. When quite pure it is perfectly colourless; in a less pure state, however, it is bright yellow. It crystallises in needles. Its solutions in water or alcohol that has been previously boiled are colourless, but they soon become yellow and red. It dissolves in alkalies, giving a beautiful carmine red solution ; this red solution may be decolourised by warming with zinc dust. Its colour appears again, however, on exposure to the air.

Braziline yields resorcin (§ 993) on dry distillation. When boiled with strong nitric acid styphnic acid (§ 1003) is formed.

Hæmatoxyline, $C_{16}H_{14}O_6,3H_2O = C_{16}H_8(OH)_6,3H_2O$, the colouring matter of logwood (*Haematoxylon Campechianum*), crystallises from water or ether in yellow prisms having a sweet taste. Its solutions are dextrorotatory. Treated with acetyl chloride it yields a hexacetate, $C_{16}H_8(O.C_3H_3O)_6$, crystallising in silky needles. It dissolves in alkalies, giving a purple red solution, which readily takes up oxygen. The ammoniacal solution rapidly darkens when exposed to the air, and leaves on evaporation *hæmateïne ammonia*, crystallising in dark violet crystals.

The solution of the latter yields a brown red precipitate of *hæmateïne*, $C_{16}H_{12}O_6$, when treated with acetic acid. Hæmateïne may also be obtained by adding a little nitric acid to an ethereal solution of hæmatoxyline. It crystallises in groups of needles and contains three molecules of water of crystallisation. Sulphurous acid or nascent hydrogen regenerates hæmatoxyline from it. Hæmatoxyline fused with potash yields much pyrogallic acid (§ 999).

1243. *Gentianine*, $C_{14}H_{10}O_5$, is extracted from the roots of *Gentiana lutea* by means of ether. It forms yellow, tasteless needles, insoluble in water, soluble in alkalies, giving an intense yellow solution.

Curcumine, $C_{10}H_{10}O_3$, is the yellow colouring matter of turmeric, from which it may best be obtained by extracting the root with benzol. It crystallises in orange yellow prisms, having a faint smell of vanilla. It is insoluble in water and melts at 165°. It is soluble in alkalies, giving a brownish red solution. Treated with boric acid an orange colour is developed, which becomes blue on subsequent addition of alkalies.

Euxanthine, $C_{19}H_{16}O_{10}$, combined with magnesia forms the principal constituent of purree, an East Indian yellow colouring matter. It may be set free from this compound by means of hydrochloric acid and recrystallised from boiling water. It forms shining yellow prisms, and is difficultly soluble in cold water, easily in alcohol and ether. It forms yellow compounds with bases. At 180° it decomposes, yielding carbonic anhydride, water, and *euxanthone :*

$$C_{13}H_8O_4.$$

The latter crystallises in yellow prisms, which are soluble in hot concentrated potash, yielding the potassium compound of *euxanthonic acid*, $C_{13}H_{10}O_5$; fused with potash, however, it is decomposed with formation of hydroquinone.

1244. *Carthamine*, $C_{14}H_{16}O_7$, occurs in safflower, the blossoms of *Carthamus tinctorius*, mixed with a yellow colouring matter soluble in water. Carthamine is of a red colour; it is soluble in alkalies and reprecipitated by acetic acid. It is soluble in alcohol. Its crystals are of a golden green colour, giving a red powder when triturated. On fusion with potash it yields paraoxybenzoic and oxalic acids.

Santaline, $C_{15}H_{14}O_5$, is the red colouring matter of sandal wood, and is extracted from it by alcohol. It forms microscopic deep red crystals, which are insoluble in water, but soluble in alkalies to a violet solution.

Carotine, $C_{18}H_{24}O$, is the red colouring matter of the carrot (*Dancus Carota*), in the cells of which it exists in red microscopic crystals. It is difficultly soluble even in boiling alcohol. It crystallises in red-brown cubes, melting at 168°.

1245. *Chrysine*, $C_{15}H_{10}O_4$, and *tectochrysine*, $C_{16}H_{12}O_4$, exist in the buds of the poplar. Chrysine crystallises in thin bright yellow tables, melting at 275° and capable of sublimation. It is insoluble in water, difficultly soluble in alcohol and ether, but readily in alkalies with yellow colour. Bromine converts it easily into *dibromo-chrysin*, strong nitric acid into *dinitro-chrysin*, $C_{15}H_8(NO_2)_2O_4$, the latter of which is only soluble in boiling strong acetic acid.

Tectochrysine, which can be separated from chrysine by solution in benzol, forms large sulphur yellow monoclinic prisms, melting at 130°.

Both bodies yield acetic acid, phenyl-methyl ketone (§ 1037), and benzoic acid when decomposed by boiling with highly concentrated potash, and from chrysine phloroglucin is also obtained. They are possibly homologues of dihydroxy-anthraquinone (§ 1197).

1246. *Chlorophyll* is the name given to the colouring matter of the green parts of plants. It occurs equally distributed in the microscopic protoplasm globules of the green plant cells, and may be extracted by alcohol, ether, and benzol. Although of such immense importance in the synthesis of organic bodies taking place in plants, very little is known about it. It is even not certain whether it contains nitrogen or not.

1247. *Picrotoxine*, $C_{12}H_{14}O_5$, is the intensely bitter constituent of *Cocculus indicus*. It may be extracted from that drug by means of hot alcohol. In the pure state it crystallises in colourless needles, difficultly soluble in water. In alkaline solution it reduces cupric salts, and yields oxalic acid when boiled with nitric acid.

Quassiine, $C_{10}H_{12}O_3$, the bitter constituent of quassia wood, crystallises from alcohol in fine, colourless, extremely bitter leaflets, which are difficultly soluble in water. At a high temperature it melts to a colourless mass.

Smilacine, from the sarsaparilla root (from the various kinds of *smilax*), forms fine colourless prisms. It is easily soluble in alcohol and ether, with difficulty in water. The aqueous solution froths readily and has a disagreeable taste.

Cascarilline, $nC_6H_9O_2$, the bitter principle of cascarilla bark, crystallises in microscopic needles, melting at 205°. It has a very bitter taste and is easily soluble in hot alcohol and ether.

Columbine, $C_{21}H_{22}O_7$, occurs, together with the alkaloid berberine and columbic acid, in the columbo root. It forms colourless, bitter prisms.

1248. *Cantharidine*, $nC_5H_6O_2$, is the blister-producing constituent of cantharides, or Spanish flies. It is found in beetles belonging to the following species: *Lytta*, *Meloë*, and *Mylabris*. It may be obtained from cantharides by extracting with ether. It crystallises in colourless prisms or leaflets, is insoluble in water, difficultly soluble in alcohol, melts at 250°, and sublimes at a lower temperature.

RESINS.

1249. The *resins*, a widely distributed class of vegetable substances, in the crude condition form amorphous masses having a conchoidal fracture, insoluble in water, soluble to different degrees in alcohol, ether, and liquid hydrocarbons, especially the terpenes, and are for the most part optically active. They melt when heated, but are not volatile without decomposition. They burn with a smoky, luminous flame.

Many of the resins occur in plants dissolved in ethereal oils. Should the vessels which contain this solution be injured, it flows out and becomes thick, or even solid, on exposure to the air, partly from evaporation of the solvent oil and partly by its oxidation. Such mixtures of oils and resins are termed *balsams*. Other resins exist suspended in the milky juice of plants mixed with gum, sugar, &c. Such juices leave, on drying up, the so-called *gum resins*. Every resin, even though it may have been purified from oily bodies by melting, and from bodies soluble in water by treatment with water solution in alcohol, ether, &c., is still a mixture of several compounds which are very difficult to separate. Several of these compounds are crystallisable when pure; all are colourless, tasteless, and odourless; many are weak acids whose alkali salts froth strongly when dissolved in water and form the *resin soaps* of commerce. Many of the resins are nearly related to the terpenes, being probably formed from those hydrocarbons by oxidation and absorption of water at the same time. Most resins when fused with potash yield resorcin (§ 993) (e.g *galbanum* and assafœtida), phloroglucin (§ 1000, e.g. dragon's blood), paraoxybenzoic acid (§ 1064, e.g. dragon's blood and gum benzoin), and protocatechuic acid (§ 1067, 2, e.g. dragon's blood, assafœtida). Fatty acids are generally formed at the same time.

Many resins are employed as medicines and in the preparation of varnishes (solutions in alcohol, turpentine, &c.), sealing wax, and similar substances. Only the more important resins will be described.

1250. *Colophony.*—When the balsams obtained from the various kinds of *Pinus, Abies*, and *Larix* are distilled with steam, turpentine passes over, and a residue is left, which when melted forms *colophony.* It is a perfectly amorphous, yellowish brown, brittle, shining mass, which is easily soluble in alcohol, ether, and oils.

Sylvic acid, or *abietic acid*, $C_{20}H_{30}O_2$, is obtained from the above resin by digesting it for a long time with alcohol, which must not be stronger than 70 per cent. On cooling the filtrate, and adding water until the liquid becomes slightly turbid, the acid crystallises out in leaflets, melting at 129°. It is soluble in ether, chloroform, and benzol, but not in water. Sylvic acid is monobasic, and yields with alkalies salts capable of crystallisation and which can be employed as soap. The salts of the other metals are insoluble. After fusion it solidifies to an amorphous mass, and is then more soluble in alcohol (pinic acid). If the alcoholic solution containing water be allowed to stand, however, the acid again becomes crystalline.

Pimaric acid, isomeric with the above, is obtained in a similar manner from the resin of *Pinus maritima.* It forms hard crusts, melting at 149°, boiling at about 320°, and is thereby converted into sylvic acid.

1251. *Copaiba Resin.*—This is obtained from the balsam of trees of the species *copaiba.* The balsam is a light yellow liquid which on distillation with water yields a terpene and the resin. The latter is a mixture of an insoluble, neutral resin and *copaibic acid*, which may be obtained in transparent prisms by evaporating the alcoholic solution. It seems to be isomeric with pimaric and sylvic acids. It can be obtained direct from the balsam by employing a concentrated aqueous solution of ammonium carbonate. It seems to be isomeric with sylvic and pimaric acids.

1252. *Guiacum* is the yellowish brown, shining resin obtained from *Guajacum officinale.* In the state of powder it becomes green on exposure to air. Its alcoholic solution is turned blue by iodine. It contains several constituents of a feebly acid nature, especially the dibasic *guaiaretic acid*, $C_{20}H_{26}O_4$, which crystallises from acetic acid in needles. It melts at about 77°, and yields *pyroguiacin*, $C_{19}H_{22}O_3$, liquid guiacol (§ 992), and cresol (§ 1016, 3), on submitting it to dry distillation.

Copal, a yellowish or brownish resin having a conchoidal fracture, is obtained from various trees growing in the East and West Indies, and also in Africa. It is decomposed on fusion, is heavier than water, almost insoluble in alcohol, soluble in ether, in which it first of all swells up. Its separate constituents have not yet been isolated.

Elemi resin, obtained from *Amarys elemifera*, *Amarys celonica*, &c., is usually met with in rather a soft condition, owing to the presence of an ethereal oil. Cold alcohol extracts an amorphous acid resin from it. Treated with hot alcohol it yields a colourless crystalline resin, amyrin, $C_{40}H_{68}O_2$, melting at 174°. *Amyrin* occurs also in animé resin.

1253. *Dammara resin* is very similar in appearance to copal, but fuses without decomposition and dissolves in boiling alcohol.

Mastic is the resin of *Pistacia Lentiscus*, a tree growing in the islands of the Greek archipelago. It occurs in small, rounded, translucent grains, and contains several constituents soluble in varying degrees in alcohol.

Olibanum, or incense, is obtained from a Boswellia growing in Abyssinia. It occurs in rounded, pale yellow grains, which on melting diffuse an aromatic perfume.

Acaroid resin is obtained from *Xanthorhoea hastilis*, a tree growing in New Holland. It yields resorcin when treated with melting potash. Nitric acid acts on it very readily, yielding picric acid in large quantities.

Dragon's blood, the resin of *Calamus Draco*, *Dracaena Draco*, and *Pterocarpus Draco*, is met with in reddish brown fragments, which yield a red powder and dissolve almost entirely in alcohol to a red solution.

Gum lac, or *lac*, exudes from punctures made by the female insects of *Coccus lacca* in twigs of several East Indian trees. It is met with in commerce in three forms—stick lac, seed lac, and shell lac. The first consists of the twigs covered with resin, the second is the resin separated from the woody substance, and the third has been purified by melting. The colour of the latter is derived from the insects.

Gum benzoin, the resin of *Styrax Benzoïn*, occurs in large brittle fragments of different shades of brown. It has a pleasant odour, resembling vanilla. It contains benzoic and frequently cinnamic acids, together with some resins of feebly acid character.

1254. *Amber* is a fossil resin formed in many peat bogs, and consists chiefly of an amorphous substance insoluble in alcohol, oils, and alkalies. It yields succinic acid in large quantities on dry distillation. Among the fossil resins may be mentioned *ozocerite*, consisting of a hydrocarbon of the C_nH_{2n} series; *fichtelite*, nC_4H_7; *xyloretin*, found in fossil fir wood; and *asphaltum*.

1255. Among the *balsams*, *storax*, from *Styrax liquidambar*, containing styrol (§ 1042), styracin (§ 1094), and cinnamic acid, *Peru balsam* and *Tolu balsam*, the former containing cinnameïn and the latter yielding toluene on dry distillation, have been already described.

Among the *gum resins* the more important are the following:—gum ammoniac, euphorbium, galbanum, gamboge, assafœtida, and myrrh; and from these resorcin, phloroglucin, paraoxybenzoic acid, and protocatechuic acid have been obtained.

1256. *Caoutchouc* and *guttapercha* consist of the dried juices of various tropical trees. The former is obtained from *Siphonia elastica*, *Hevea caoutchouc*, &c., the latter from various isonandras growing in the East Indies.

Caoutchouc consists mainly of a hydrocarbon of the formula nC_4H_7, a white substance which may be obtained pure by treatment of the crude substance with water, alcohol, and alkalies; the residue is then dissolved in chloroform and precipitated by alcohol. The substances also occurring in raw caoutchouc are albuminous matters and the methyl derivatives of dambose (§ 876).

Raw caoutchouc softens on warming, and may be kneaded and mixed with foreign substances. When kneaded with sulphur and heated, vulcanised caoutchouc is formed.

Raw guttapercha is tolerably hard at ordinary temperatures, but softens below 100° and may also be vulcanised. Its principal constituent is a hydrocarbon of the formula nC_5H_8, which may be obtained pure by treating with boiling ether. It forms a white powder melting at 100°.

ALKALOIDS.

1257. In most poisonous plants there exist certain basic substances of a highly poisonous nature. They are found in the plant in combination with acids, and have been called *alkaloids*. They all contain nitrogen, and combine with acids, forming salts, just as ammonia does. Only a few contain no oxygen, and these are generally capable of distillation. As a rule they contain oxygen, are not volatile without decomposition, and are crystallisable. Their basic properties differ widely. They are mostly soluble with difficulty in water, more readily in alcohol, ether, amyl alcohol, chloroform, benzene, &c. They generally possess a bitter taste, and very many of them are optically active.

In order to prepare them the plants are usually extracted with water or dilute mineral acids, and the solution treated with ammonia or other strong base. The volatile alkaloids may then be distilled off in steam, while the nonvolatile ones are precipitated.

As a rule several alkaloids are contained in the same plant together with other substances, so that their isolation is frequently a troublesome and tedious matter.

All alkaloids are precipitated by phospho-molybdic acid and by the double iodides of potassium with mercury and cadmium. Many of them may be precipitated by a solution of iodine in iodide of potassium and by platinic and auric chlorides.

Volatile Alkaloids containing no Oxygen.

1258. *Conine*, $C_8H_{15}N = C_8H_{14} : NH$, occurs in hemlock (*Conium maculatum*). To obtain it the crushed seeds are distilled with dilute potash, the distillate neutralised with sulphuric acid and evaporated to a syrup. On addition of alcohol ammonium sulphate is precipitated; the filtrate is evaporated and then distilled with concentrated potash. The oily conine which floats on the watery distillate is separated, and allowed to remain in vacuo for some time to remove ammonia, and finally purified by distillation.

Conine is a colourless, highly poisonous oil, having the odour of hemlock. It boils at 168° and its sp. gr. at 0° is 0·886. It mixes in all proportions with alcohol and ether. It is dextrorotatory, dissolves in 100° parts of water, giving a strongly alkaline solution. Water dissolves in it to a slight extent, more being dissolved by the cold substance than when it is warm. It is monobasic and yields crystalline, generally deliquescent salts, which oxidise when exposed to air, becoming brown at the same time. The hydrochloride has the formula $C_8H_{14}:NH_2Cl$.

With iodides of the alcohol radicals it yields crystalline compounds. With ethyl iodide the substance produced is $C_8H_{14}:N(C_2H_5).HI$.

These compounds are decomposed by alkalies, the iodides being regenerated. They are capable of uniting with yet another molecule of the iodides, forming salts of the general formula $C_8H_{14}N(R)_2I$, which are not decomposed by alkalies, but yield caustic bases with freshly precipitated argentic hydrate. The ethyl compound has the composition $C_8H_{14}N(C_2H_5)_2OH$. This behaviour on the part of conine shows that it contains the imide group (§ 265).

On oxidation with nitric acid or chromic acid conine yields normal butyric acid. Treated with nitrous anhydride and subsequently with water, it yields *azoconydrin*, $C_8H_{16}N_2O$, a yellowish oil, which yields a homologue of acetylene, allylene, &c., on treatment with phosphoric pentoxide. This substance is named *conylene* $= C_8H_{14}$; it boils at 126° and combines with bromine, producing *conylene dibromide:*

$$C_8H_{14}Br_2.$$

Methyl conine, $C_8H_{14}:N.CH_3$, occurs, together with conine, in the seeds of the hemlock. *Conydrin*, $C_8H_{17}NO$, is also present; it is a crystalline, strongly basic alkaloid, melts at 121° and boils at 240°. It is converted by phosphoric anhydride into conine.

Paraconine, $C_8H_{15}:N$, isomeric with conine, is obtained by heating dibutyraldin (§§ 424 and 763), isomeric with conydrin, with a small quantity of alcohol to between 130° and 180°. It is very similar to conine, but is not an imide base, as it does not yield an analogous compound to that obtained from conine on treatment with the iodide of an alcohol radical. It, however, yields the iodide of an ammonium base, from which the hydrate may be prepared by the action of argentic hydrate.

1259. *Nicotine*, $C_{10}H_{14}N_2$, the alkaloid of tobacco, in the leaves and seeds of which it exists, may be isolated similarly to conine. It is purified by distilling from quick-lime in a stream of hydrogen.

Nicotine is a colourless liquid which turns brown on exposure to air. It is soluble in alcohol, ether, and water. Its specific gravity is 1·048 and vapour density 5·618. The odour is similar to that of tobacco. It yields difficultly crystallisable salts with acids. The hydrochloride is $C_{10}H_{14}N_2.2HCl$. The iodide unites with iodine, forming a difficultly soluble, crystalline periodide. The haloid salts yield well-crystallised double salts with haloid metallic derivatives; for example, $C_{14}H_{10}N_2.2HCl.PtCl_4$, $C_{10}H_{14}N_2.HCl + 4HgCl_2$, &c. Free nicotine also forms compounds with haloid salts of metals; $C_{10}H_{14}N_2.3HgCl_2$, $C_{10}H_{14}N_2.HgI_2$, &c.

If bromine be added to an ethereal nicotine solution, a compound having the formula $C_{10}H_{12}Br_2N_2.HBr.Br_2$ is formed, which on boiling with water or alcohol gives up two atoms of bromine and yields a salt of *dibromonicotine*. The base $C_{10}H_{12}Br_2N_2$ is precipitated by ammonia in the form of colourless needles which have feebly basic properties.

Nicotine is a nitrile base, as its compounds with the iodides of alcohol radicals yield, on treatment with argentic hydrate, strongly caustic, nonvolatile bases, $C_{10}H_{14}(C_2H_5)_2N_2(OH)_2$.

When oxidised by chromic acid it yields an amidated acid, $C_6H_5NO_2$, which distilled from lime gives rise to an oily base, C_5H_5N, soluble in water. The latter is pyridine.

1260. *Sparteine*, $C_{15}H_{26}N_2$, from *Spartium scoparium* (§ 1237), is obtained like the preceding alkaloids. It is a thick, colourless oil, boiling at 288°. It is only slightly soluble in water, is strongly alkaline, and resembles nicotine in its compounds. Like nicotine, it is a nitrile base.

Alkaloids containing Oxygen.

Opium Bases.

1261. Opium, the dried juice of the poppy (*Papaver somniferum*), contains a large number of crystalline alkaloids, mostly combined with meconic acid (§ 943), in addition to resins and other substances. The best known among the alkaloids are morphine, codeïne, thebaïne, papaverine, narcotine, and narceïne.

Morphine, the most important of them all, and narcotine are those present in greatest quantity.

There are several ways of separating the alkaloids; that about to be described gives especially good results.

The salts of the alkaloids present in the opium are first of all extracted by water at a temperature of 65°; the solution is then treated with barium chloride, the precipitated barium meconate filtered off, the filtrate concentrated by evaporation and left to crystallise. The hydrochlorides of morphine and codeïne then crystallise out; they are collected, pressed, and then decomposed by the addition of ammonia. Morphine is precipitated, the filtrate concentrated by evaporation, and codeïne precipitated by means of concentrated potash, which retains in solution any morphine which is still present. The dark brown mother liquors from both alkaloids are then made alkaline and supersaturated with ammonia. A precipitate of narcotine, papaverine, and thebaïne is obtained, while narceïne and meconine remain in solution. The filtrate is treated with plumbic acetate, the precipitate filtered off, and the filtrate treated with sulphuric acid to remove lead; on saturating the filtrate from the lead sulphate with ammonia, and then evaporating, narceïne crystallises out. Meconine remains in solution, and may be obtained by shaking the solution with ether.

The crystalline magma, consisting of narcotine, papaverine, and thebaïne, contaminated with some resin, after being repeatedly washed with water, is boiled with alcohol; narcotine and papaverine separate out on cooling. The mixture of the two is then treated with concentrated potash, which is diluted with water after standing some time; narcotine remains undissolved. The alkaline mother liquors are then neutralised, evaporated to dryness, and treated with acetic acid, which dissolves the papaverine. It can now be precipitated by ammonia from the solution.

The alcoholic solution containing thebaïne is evaporated and the residue taken up with hot acetic acid. There still remain small quantities of narcotine, papaverine, and resin, which are precipitated out by plumbic acetate, the filtrate treated with sulphuric acid to remove lead. Thebaine may be precipitated from the filtered liquid by ammonia.

If it be necessary to isolate only morphine and narcotine, the opium is treated with dilute alcohol until nothing more is dissolved, and the bases precipitated by ammonia, leaving the whole to stand for some time. The narcotine may now be separated from the morphine by means of potash, in which the former is insoluble, the latter soluble. The morphine is precipitated from the solution on addition of ammonium carbonate.

The separated alkaloids are finally purified by recrystallising them either in the free state or in the form of salts.

1262. *Morphine*, $C_{17}H_{19}NO_3,H_2O$, crystallises from alcohol in colourless lustrous prisms, which are soluble in 500 parts of boiling water, easily soluble in ethyl and amyl alcohols, but insoluble in ether or chloroform. It is readily soluble in caustic alkalies, but scarcely at all in solution of ammonia. It is lævorotatory and tastes slightly bitter.

It is a nitrile base, and combines with one equivalent of an acid to form crystalline salts, soluble in water and alcohol; e.g.

$$C_{17}H_{19}NO_3.HCl,3H_2O.$$

They give a yellow precipitate with platinic chloride:

$$(C_{17}H_{19}NO_3.HCl)_2PtCl_4.$$

Solutions of neutral morphine salts are coloured blue by neutral ferric chloride solution. The alkaloid dissolves in warm concentrated sulphuric acid, giving a dirty red colour; on addition of a little nitric acid the colour is changed to purple red. Aqueous solutions of iodic acid are reduced by morphine and its salts, free iodine being liberated. It is decomposed at 200° by concentrated potash and yields methylamine.

If a solution of the hydrochloride of morphine be treated with argentic nitrite at 60° a base is obtained which sometimes occurs in opium. This base is *oxymorphine*, $C_{17}H_{19}NO_4$. Its difficultly soluble compound with hydrochloric acid is decomposed by ammonia, yielding the free base as a shining, white, crystalline powder, insoluble in water, alcohol, and ether.

If morphine be heated to 150° with concentrated hydrochloric acid, and soda afterwards added, a white amorphous powder, consisting of *apomorphine*, $C_{17}H_{17}NO_2$, is obtained. Exposed to air it rapidly becomes green; it is soluble in alcohol, ether, and chloroform. It acts as an emetic.

1263. *Codeïne*, $C_{18}H_{21}NO_3$, homologous with morphine, crystallises from ether in large octahedra containing no water. When crystallised with a molecule of water it takes the form of rhombic prisms. It dissolves in 80 parts of water at 15° and also easily in alcohol. Its melting point is 150°. It forms crystalline salts, soluble in water. If the hydrochloride be heated with a saturated solution of zinc chloride to 170°, it loses a molecule of water and a salt of *apocodeïne* is obtained. Soda precipitates the free base:

$$C_{18}H_{19}NO_2,$$

as an amorphous resin. Heated to 150° with strong hydrochloric acid, codeïne yields water, methyl chloride, and apomorphine.

1264. *Thebaïne*, $C_{19}H_{21}NO_3$, crystallises in silvery quadratic tablets, melting at 193°. Concentrated sulphuric acid dissolves it, giving a deep red colour; it is also soluble in alcohol and ether, but not in water, potash, or ammonia. On boiling it with hydrochloric acid it yields a salt of *thebenine*, which is isomeric with thebaïne. It is amorphous.

Papaverine, $C_{21}H_{21}NO_7$, crystallises in colourless prisms, insoluble in water and melting at 147°.

1265. *Narcotine*, $C_{22}H_{23}NO_7$, forms lustrous, tasteless prisms, which melt at 176° and decompose at 220°. It is insoluble in water and alkalies, soluble in alcohol and ether, acts as a narcotic, but is less poisonous than morphine. Its salts contain one equivalent of acid, do not generally crystallise well, and have an intensely bitter taste.

Concentrated sulphuric acid dissolves narcotine in the cold with yellow colour; when heated the solution becomes blood red; the same change takes place on the addition of a little nitric acid.

Long boiling with water splits up narcotine into meconine and cotarnine; heated with manganese dioxide and sulphuric acid, it yields opianic acid and cotarnine; with dilute nitric acid it yields in addition meconine, hemipinic acid, and other bodies.

Heated with water to 250°, much trimethylamine is formed. At high temperatures narcotine, when treated with dilute sulphuric or hydrochloric acid, is decomposed, losing three methyl groups one after the other, the three following bases being produced: $C_{21}H_{21}NO_7$, $C_{20}H_{19}NO_7$, and $C_{19}H_{17}NO_7$.

Cotarnine, $C_{12}H_{13}NO_3,H_2O$, a monobasic alkaloid, crystallises in shining prisms grouped into stars, which are soluble in water, alcohol, and ammonia, and melt at 100°. On boiling with very dilute nitric acid it yields *cotarnic acid*, $C_{11}H_{12}O_5$, and *apophylenic acid*, $C_8H_7NO_4$, together with methylamine.

Meconine, $C_{10}H_{10}O_4$, forms shining colourless crystals, melting at 110°, difficultly soluble in water. When heated with acid, ethereal meconine derivatives are produced.

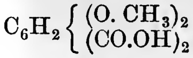
Opianic acid, $C_{10}H_{10}O_5$, crystallises in needles melting at 140°. It dissolves but little in water. On oxidation it yields hemipinic acid. Heated with potash, meconine and hemipinic acids are produced:

$$2C_{10}H_{10}O_5 + 2KHO = C_{10}H_8K_2O_6 + C_{10}H_{10}O_4 + 2H_2O.$$

Concentrated sulphuric acid at 180° converts it into rufiopin (§ 1169, 2).

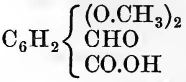
Hemipinic acid, $C_{10}H_{10}O_6$, crystallises from hot water in four-sided prisms capable of sublimation, and which contain varying amounts of water of crystallisation. It forms acid and neutral salts, those of potassium being $C_{10}H_9KO_6$ and $C_{10}H_8K_2O_6$. When hemipinic acid is heated with hydrochloric, hydrobromic, or hydriodic acids it is decomposed, giving rise to methyl chloride or bromide, carbonic anhydride, and two isomeric acids, *opinic acid* and *isopinic acid*, having the formula $C_{14}H_{10}O_8,3H_2O$.

Hemipinic acid is represented by the formula :



$$C_6H_2\left\{\begin{array}{l}(O.CH_3)_2\\(CO.OH)_2\end{array}\right.$$

being a carboxylated dimethyl protocatechuic acid, opianic acid having one of the carboxyl groups replaced by the aldehyde group, thus :



$$C_6H_2\left\{\begin{array}{l}(O.CH_3)_2\\CHO\\CO.OH\end{array}\right.$$

1266. *Narceine*, $C_{23}H_{29}NO_9$, crystallises in white interlaced needles. It melts at 145°. It is insoluble in ether, difficultly soluble in water and cold alcohol. It is coloured blue by a small quantity of iodine, similarly with starch. Its crystallisable salts are decomposed by water into acid and base.

Other alkaloids are found in small quantities in the various kinds of opium. Among these are *hydrocotarnine*, $C_{12}H_{15}NO_3$; *codamine*, $C_{19}H_{23}NO_3$ (a hydrothebaïne?); *laudamine*, $C_{20}H_{25}NO_4$; *protopine*, $C_{20}H_{19}NO_5$; *meconidine*, $C_{21}H_{23}NO_4$ (hydropapaverine?); *cryptopine*, $C_{21}H_{23}NO_5$; *laudanosine*, $C_{21}H_{27}NO_4$; *rhœadine*, $C_{21}H_{21}NO_6$, &c.

Rhœadine is found chiefly in the field poppy (*Papaver Rhoeas*).

Cinchona Bases.

1267. In the true cinchona barks there exist two bases, *quinine*, $C_{20}H_{24}N_2O_2$, and *cinchonine*, $C_{20}H_{24}N_2O$, in varying quantity, together with quinic and quinotannic acid and cinchona red (§ 1230).

The *calisaya* bark contains the most alkaloids, between 2 and 3 per cent. of quinine and perhaps a tenth of that quantity of cinchonine.

The bark of *China Huanaco*, however, contains about 2¼ per cent. of cinchonine and about 0·8 per cent. of quinine. In many cinchona barks the alkaloids present in largest quantity are quinidine and cinchonidine, isomeric with those above mentioned.

In order to isolate the bases the pulverised bark must be extracted with very dilute hydrochloric acid, and the filtrate precipitated with soda. The alkaloids may then be extracted from the pressed precipitate by boiling alcohol and separated by conversion into sulphates, that of quinine being the most difficultly soluble, or by means of ether, which does not dissolve cinchonine. The alkaloids may be precipitated in the colourless state by addition of ammonia to solutions of their salts previously decolourised by animal charcoal. Long heating with excess of acid must be carefully avoided, or the alkaloids will be converted into resinous isomers, quinicine, and cinchonicine.

1268. *Quinine*, $C_{20}H_{24}N_2O_2.3H_2O$, is precipitated from its salts as a white powder. It crystallises from ether or chloroform in colourless needles, which lose their water of crystallisation on heating and eventually fuse into a resinous mass. It dissolves in about 900 parts of boiling water, but requires 1,600 parts of water at 20° to dissolve it.

It is very easily soluble in alcohol, and the solution is lævorotatory. It has an alkaline reaction and, like its salts, an intensely bitter taste. It combines with one or two equivalents of acid, the latter having an acid reaction. $2(C_{20}H_{24}N_2O_2,HCl),3H_2O$ crystallises in long silky needles, which are tolerably soluble in water. $C_{20}H_{24}N_2O_2.2HCl$ is converted by water into the preceding salt, but yields with platinic chloride a stable double salt of a yellow colour, which soon becomes crystalline:

$$C_{20}H_{24}N_2O_2,2HCl,PtCl_4,H_2O.$$

Quinine sulphate, $(C_{20}H_{24}N_2O_2)_2H_2SO_4$, crystallises from hot water in needles containing $7\frac{1}{2}$ molecules of water. It is efflorescent. From alcohol it crystallises with $2H_2O$. It is the salt of quinine most used as a febrifuge. It is easily dissolved by dilute sulphuric acid, forming a salt containing only half the quinine that the other does, $C_{20}H_{24}N_2O_2.H_2SO_4,7H_2O$; this crystallises in transparent four-sided prisms, and dissolves to a solution having a blue fluorescence. It is soluble in 11 times its weight of water.

The neutral sulphate is also readily soluble in acetic acid, and yields, on addition of iodine solution, *quinine sulphate diiodide*, or *herapathite*, crystallising in large thin tables, which are almost colourless by transmitted light, but exhibit a fine beetle green colour when viewed by reflected light, $C_{20}H_{24}N_2O_2,H_2SO_4.I_2 + 5H_2O$.

Quinine forms crystalline compounds with iodides of alcohol radicals which are not decomposed by alkalies, but yield caustic alkylquinine hydrates when decomposed by argentic hydrate. It is therefore a nitrile base. With the chlorides of the acid radicals anhydrous quinine yields hydrochlorides of quinine salts, from which the latter may be precipitated as amorphous masses. *Benzoyl-quinine* has the formula $C_{20}H_{23}(C_7H_5O)N_2O_2$.

If chlorine water be added to a quinine solution, and afterwards ammonia, an emerald green colour is developed; ferrocyanide of potassium and ammonia give a deep red colour.

1269. *Cinchonine*, $C_{20}H_{24}N_2O$, is precipitated from solutions of its salts in an earthy condition; it is, however, readily obtained in shining prisms by crystallising from alcohol. It is less soluble in alcohol and water than quinine, is quite insoluble in ether, and is dextrorotatory. Its salts correspond to those of quinine, but are more readily soluble in water. Chloro-substitution products are obtained on addition of chlorine water and ammonia in form of a yellow precipitate. If bromine be added to the hydrochloride of cinchonine, and the resulting salt of *dibromo-cinchonine* decomposed by ammonia, the brominated compound $C_{20}H_{22}Br_2N_2O$ is formed; on boiling this dibromo-cinchonine with potash *oxycinchonine* $C_{20}H_{24}N_2O_2$ is produced. Although this substance has the same composition as quinine it differs markedly from it in its properties.

Acetate of cinchonine dissolved in alcohol yields, when treated with sodium amalgam, colourless scales of *dihydro-cinchonine:*

$$C_{20}H_{26}N_2O,$$

and amorphous *tetrahydro-cinchonine*, $C_{20}H_{28}N_2O$.

1270. A dark brown amorphous mass, called *quinoïdine*, is obtained from the last mother liquors of quinine and cinchonine; from it the two alkaloids quinidine and β-cinchonine have been prepared.

Quinidine, $C_{20}H_{24}N_2O_2,2H_2O$, which occurs in quantity in pitayochina, crystallises from alcohol in large efflorescent prisms, melting at 168°. Like quinine it gives a green solution with ammonia and chlorine water. Quinidine salts are more easily soluble in water than those of quinine.

Cinchonidine, $C_{20}H_{24}N_2O$, is found more especially in Bogatachina. It forms large glassy crystals, the solution of which is lævorotatory. *β-Cinchonine*, $C_{20}H_{24}N_2O$, occurs with quinidine in quinoïdine and is dextrorotatory.

1271. On heating the sulphates of the quinia alkaloids with a little nitric acid to 130° they yield salts of two resinous amorphous bases. *Quinicine* is obtained from quinine and quinidine, while cinchonine and cinchonidine yield *cinchonicine*. They are isomeric with the bases from which they are produced.

In some cinchona barks the following alkaloids occur:—

Quinamine, $C_{20}H_{26}N_2O_2$; *paytine*, $C_{21}H_{24}N_2O_2$; and *aricine*, $C_{23}H_{26}N_2O_4$.

1272. A homologous series of bases, the *chinoline bases*, are produced by dry distillation of quinine, cinchonine, and their isomers with potash. They are also products of the dry distillation of coal.

Chinoline, C_9H_7N, boils at 238°.
Lepidine, $C_{10}H_9N$ „ 269°–271°.
Cryptidine, $C_{11}H_{11}N$ „ about 274°.

They are nitrile bases, as their alkyl-iodo compounds are only decomposed by silver oxide; they then yield caustic ammonium hydrate bases. With acids they form neutral salts easily soluble in water.

Their amyl-iodo compounds when heated with potash yield tabular crystals having a fine beetle-green lustre, soluble in alcohol without decomposition. They are blue colouring matters and have been called *cyanines*.

$$2(C_9H_7N.C_5H_{11}I) + KHO = KI + H_2O + C_{28}H_{35}N_2I$$

(Chinoline cyanine).

$$2(C_{10}H_9N.C_5H_{11}I) + KHO = KI + H_2O + C_{30}H_{39}N_2I$$

(Lepidine cyanine).

The cyanines combine with 2 equivalents of acid, forming colourless salts.

1273. *Bases from Strychnos.*—In different varieties of Strychnos, especially in the seeds of *S. nux vomica* and *S. Ignatii* (St. Ignatius bean), two extremely bitter and poisonous alkaloids occur—*strychnine*, $C_{21}H_{22}N_2O_2$, and *brucine*, $C_{23}H_{26}N_2O_4$.

In order to prepare them the seeds are boiled with concentrated alcohol, dried, powdered, and repeatedly extracted with dilute alcohol. The alcohol is evaporated from the extract and the aqueous residue precipitated with plumbic acetate, the lead removed from the filtrate with sulphuretted hydrogen and the bases precipitated from the clear solution by addition of magnesia. After standing for eight days the precipitate is treated with cold alcohol to remove brucine, and the strychnine, which is nearly insoluble in that solvent, recrystallised from boiling spirits of wine.

1. *Strychnine*, $C_{21}H_{22}N_2O_2$, forms colourless tetragonal prisms, which are nearly insoluble in water, absolute alcohol, and ether, but more readily dissolved by hot aqueous alcohol, benzene, or chloroform. The solutions are optically lævorotary. The crystallisable salts, e.g. the nitrate, $C_{21}H_{22}N_2O_2.HNO_3$, which crystallises in tufts of needles, dissolve readily in water, at least when hot, and on addition of ammonic sulphocyanate give a crystalline precipitate of strychnine sulphocyanate. Strychnine dissolves in cold sulphuric acid, forming a colourless liquid, which on addition of potassic dichromate yields a beautiful bluish violet coloration. Strychnine chromate, which is insoluble in water, shows this reaction when treated with sulphuric acid.

2. *Brucine*, $C_{23}H_{26}N_2O_4,4H_2O$, crystallises in plates or prisms, is less poisonous than strychnine, and dissolves more readily in water and alcohol, yielding lævorotary solutions. Concentrated nitric acid colours strychnine first red, then yellow. On addition of stannous chloride the colour changes to deep violet. On heating brucine with manganic oxide and sulphuric acid methylic alcohol distils over.

1274. *Bases from Veratrum.*—Sabadilla seeds (from *V. Sabadilla*) contain a veratrine salt of veratric acid; hellebore (from *V. album*) contains veratrine and jervine. The procedure for preparing these alkaloids is similar to that for strychnine and brucine, the separation of the two alkaloids being effected by dilute sulphuric acid, which gives a readily soluble salt with veratrine, that of jervine being difficultly soluble.

1. *Veratrine*, $C_{32}H_{52}N_2O_8$, is obtained either as a light powder or as prisms which effloresce in air. It melts at 115° and solidifies on cooling to a resinous mass. It dissolves readily in alcohol and ether, but is nearly insoluble in water. When a trace is brought into contact with the nose it causes violent sneezing; when swallowed it acts as a violent poison. It dissolves in sulphuric acid, the solution having a yellow colour, which slowly becomes blood red, the same change being effected quickly on heating. It unites with one equivalent of acid to form salts that are in part crystallisable.

2. *Jervine*, $C_{30}H_{46}N_2O_3,2H_2O$, forms prisms, insoluble in water, readily soluble in alcohol, and with acids yields salts which are generally soluble.

1275. *Berberine* and *oxyacanthine* occur in the roots of *Berberis vulgaris*, the first in numerous other plants also, such as Colombo root, in different menispermia and ranunculaceæ.

Berberine, $C_{20}H_{17}NO_4,6H_2O$, forms yellow needles; it melts, when anhydrous, at 120°, is soluble in water, and gives yellow crystalline salts with acids, which are precipitated from their solutions by addition of an excess of acid. Nascent hydrogen converts it into *hydroberberine*, $C_{20}H_{21}NO_4$, forming small crystals of adamantine lustre, reoxidised by nitric acid to berberine.

Oxyacanthine, $C_{32}H_{46}N_2O_{11}$ (?), crystallises from ether in colourless prisms, turning yellow on exposure to light.

1276. *Piperine*, $C_{17}H_{19}NO_3$, the alkaloid of the different kinds of pepper, is best prepared from white pepper. This is extracted with alcohol, the solvent evaporated, the extract washed with water, lime or potash added, and the result again extracted with alcohol. On evaporation piperine crystallises. It forms colourless tetragonal plates, destitute of odour or taste, is insoluble in water, readily soluble in alcohol or ether. The alcoholic solution has a sharp peppery taste. The salts of piperine are decomposed by water.

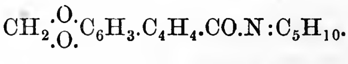
On boiling with alcoholic potassic hydrate it splits up into piperic acid and piperidine.

Piperidine, $C_5H_{11}N = C_5H_{10}:NH$, is a strongly alkaline liquid, miscible with water and alcohol. It boils at 106° and has vapour density 2·97. Its salts crystallise well. Heated at 300° for several hours with concentrated sulphuric acid it yields pyridine (§ 892). It unites with the alkyl iodides, forming alkyl-piperidine iodides, from which the alkyl-piperidines can be separated as strongly alkaline bases which can be distilled. *Methyl piperidine*, $C_5H_{10}:N.CH_3$, boils at 118°, *ethyl piperidine* at 128°. These again unite with alkyl iodides to form salts, from which the caustic, non-volatile dialkyl piperidinammonic hydrates can only be obtained by the action of argentic hydrate. With benzoyl chloride piperidine yields crystalline *benzoyl piperidine*, $C_5H_{10}:N.CO.C_6H_5$.

Piperic acid, $C_{12}H_{10}O_4 = CH_2\genfrac{}{}{0pt}{}{\cdot O\cdot}{\cdot O\cdot}C_6H_3.C_4H_4.CO.OH$, is obtained by addition of hydrochloric acid to the potassic salt; it crystallises from alcohol in clear yellow interlaced needles, melts at 216°, and is nearly insoluble in water. With bromine it yields *piperic acid tetrabromide*, $C_{12}H_{10}Br_4O_4$, which on heating with dilute solution of potassic hydrate yields piperonal (§ 1034), as does also potassic piperate when distilled with potassic permanganate. On fusing with potassic hydrate piperic acid is decomposed into potassic acetate, oxalate, carbonate, and protocatechuate. It unites with nascent hydrogen, forming

Hydropiperic acid, $C_{12}H_{22}O_4$, which crystallises in fine needles, melts at 70°–71°, and unites with bromine to form hydropiperic acid dibromide, $C_{12}H_{12}Br_2O_4$.

From this it can scarcely be doubted that piperic acid possesses the structural formula $CH_2\genfrac{}{}{0pt}{}{\cdot O\cdot}{\cdot O\cdot}C_6H_3.CH:CH.CH:CH.CO.OH$, piperine being its piperidine derivative corresponding to benzoyl piperidine:

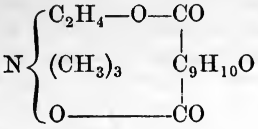


$$CH_2\genfrac{}{}{0pt}{}{\cdot O\cdot}{\cdot O\cdot}C_6H_3.C_4H_4.CO.N:C_5H_{10}.$$

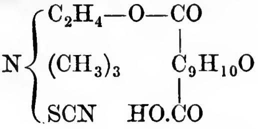
1277. *Sinapine*, $C_{16}H_{23}NO_5$, occurs as sulphocyanate in the seeds of *Sinapis alba*, and is only known in the form of its salts. Mustard flour is pressed and washed with cold alcohol to remove any fatty oils, and then extracted with boiling 85 % alcohol. On evaporating the alcohol and removing the layer of fat from the aqueous solution, *sinapine sulphocyanate*, $C_{16}H_{23}NO_5.HSCN$, crystallises from this latter and is purified by pressing and recrystallisation from boiling alcohol. It forms light fine needles and melts at 130°; on addition of sulphuric acid it is converted into the acid sulphate:

$$C_{16}H_{23}NO_5.H_2SO_4,2H_2O,$$

from which sinapine can be liberated by addition of baryta water. On evaporation, especially when alkaline, the resulting solution decomposes into choline (sincaline, § 525) and the dibasic *sinapic acid*, $C_{11}H_{12}O_5 = C_9H_{10}O\genfrac{}{}{0pt}{}{.CO.OH}{.CO.OH}$. This latter crystallises in prisms, cannot be sublimed, and is difficultly soluble in water and alcohol at the ordinary temperature. Sinapine therefore appears to be a saline compound of choline and sinapic acid :



the sulphocyanate :



1278. *Atropine*, $C_{17}H_{23}NO_3$, occurs in the deadly nightshade, (*Atropa Belladonna*) and in *Solanum nigrum.* It is prepared from belladonna by heating the freshly expressed and filtered sap to 90°, addition of potash, and shaking with chloroform. It crystallises in prisms of sharp and bitter taste, melts at 90°, is difficultly soluble in cold water, readily in alcohol. Either free or in the form of its salts it causes, even in extremely small quantity, dilatation of the pupil of the eye. On boiling with bases and acids it splits up into tropic acid (§ 1084, 2) and *tropine*, $C_8H_{15}NO$, an alkaloid readily soluble in water, alcohol, and ether, crystallising in tables of m.p. 61°.

Hyoscyamine, $C_{17}H_{23}NO_3$, isomeric with the above, occurs in the seeds, &c., of *Hyoscyamus niger* and *H. albus*, and appears to be identical with the alkaloid formerly described as *daturine* (from *Datura Stramonium*). It crystallises in silky needles; it dilates the pupil, and on heating with baryta is decomposed into tropine and tropic acid. From this the relations of hyoscyamine and atropine must be very close; they are probably physical isomerides.

Physostigmine, or *eserine*, $C_{15}H_{21}N_3O_2$, is the alkaloid of the Calabar bean (from *Physostigma venenosum*). It is a yellow, amorphous, strongly alkaline mass, causing contraction of the pupil. It oxidises on exposure to air, as do also the aqueous solution of its salts.

1279. *Cocaine*, $C_{17}H_{21}NO_4$, the alkaloid of the leaves of *Erythroxylon Coca*, crystallises in monoclinic prisms and melts at 98°. On heating with hydrochloric acid it splits up into benzoic acid, methylic alcohol, and an alkaloid *ecgonine*, $C_9H_{15}NO_3$. This latter is readily soluble in water, insoluble in ether, and crystallises with one molecule H_2O in shining prisms, melting at 198°.

Colchicine, $C_{17}H_{19}NO_5$, occurs in all parts of *Colchium autumnale*; it is amorphous, soluble in water and alcohol, and possesses a sharp and bitter taste. It melts at 140°, is very poisonous, and scarcely possesses basic properties.

Solanine, $C_{42}H_{87}NO_{16}$, occurs in various solonaceous plants, and especially in potatoes that have sprouted in the dark. It is extracted by dilute sulphuric acid, and on quick precipitation of the filtrate with ammonia and recrystallisation of the precipitate from boiling alcohol is obtained in silky prisms, melting at 235°, of weak basic properties and nearly insoluble in water; its salts are gummy. Even traces of it impart a fine red colour to a warm mixture of alcohol and sulphuric acid. Solanine is a *glucoside alkaloid*, as on boiling with dilute mineral acids it takes up water and decomposes into sugar and the more strongly basic *solanidine*, $C_{26}H_{41}NO_2$. The latter crystallises in fine needles, melts at 200°, and can be sublimed without much decomposition. Its salts crystallise readily.

1280. The seeds of *Peganum harmala*, a plant growing on the Russian steppes, contain *harmaline*, $C_{13}H_{14}N_2O$, crystallising in rhombic pyramids, and *harmine*, $C_{13}H_{12}N_2O$, crystallising in shining prisms, and which can also be prepared by oxidation of the former. They are both monacid bases.

Of other alkaloids there may be mentioned—

Aconitine, $C_{30}H_{47}NO_7$, from monk's hood (*Aconitum Napellus*).

Bebeerine, $C_{19}H_{11}NO_3$, in the bark of *Nectandra Rodiei.*

Chelidonine, $C_{19}H_{17}NO_4$, and *chelerythrine*, $C_{19}H_{17}N_3O_3$, in *Chelidonium majus.*

Curarine, contained in the South American arrow poison.

Delphinine, $C_{24}H_{35}NO_2$, in *Delphinium Staphisagria*, and finally caffeine and theobromine, which have been already described (§ 931).

BILE DERIVATIVES.

1281. The gall bladder of animals contains a green or brown liquid, of faint alkaline reaction and bitter taste. This has been formed in the liver, and contains, in addition to mucus, choline, lecithine, fatty soaps, and paralactic acid, the sodic, or more rarely the potassic, salts of the *bile acids*, *cholesterine*, and the *bile pigments.* The latter and cholesterine occur at times so richly in the liver that they crystallise out in the gall bladder and form gall stones.

Bile Acids.

1282. In the bile of most animals *two* bile acids are found, which are both monobasic and contain nitrogen, but only one contains sulphur. On boiling with acids or alkalies the two acids from the same animal yield the nitrogen-free acid, *cholic acid*; in the case of the bile acid free from sulphur, *glycocholic acid*, glycine (§ 717) is also obtained, whilst from the sulphur-containing acid, *taurocholic acid*, the second product is taurine (§ 528). All bile acids, even when present in very small quantity, give '*Pettenkofer's reaction*,' i.e. a beautiful purple coloration, on addition of a little sugar and then of concentrated sulphuric acid. This coloration occurs most readily at about 60°.

The alkali salts occurring in the bile are readily soluble in water and alcohol, but insoluble in ether. In order to obtain them in a state of purity the bile is mixed with so much animal charcoal that, on evaporating to dryness on the water bath, a dry powder remains, from which absolute alcohol extracts the now colourless salt of the bile acids, together with cholesterine, choline, lactic acid, &c. On addition of ether containing some water, the salts of the bile acids are precipitated as a colourless plaster-like mass, which crystallises on long standing in the liquid and forms the crude material for preparing the acids.

The *acids of ox gall* have been best investigated; they occur also in the bile of man, of the dog, and of most animals that have been investigated as yet, the proportion of the sulphurised acid to that free from sulphur generally differing. They are designated by the name given above.

1283. *Glycocholic acid*, $C_{26}H_{43}NO_6$. On addition of dilute sulphuric acid to an aqueous solution of the crystallised salts obtained as above described, a colourless precipitate is obtained, which after some time—especially when the water contains some ether—changes into a voluminous magma of fine white needles. Collected on a filter, it contracts on drying to a shining mass of interlaced needles.

Glycocholic acid is little soluble in water, more readily in alcohol; it has a faint acid reaction, a bitter-sweet taste, and is dextrorotary ($[\alpha] = + 25{\cdot}7°$). It yields salts of neutral reaction, of which the alkali salts are readily soluble in water, those of the other metals mostly difficultly soluble in water, more readily in alcohol. The sodic salt, $C_{26}H_{42}NaNO_6$, forms fine prisms; addition of plumbic acetate to its aqueous solution precipitates the lead salt, $(C_{26}H_{42}NO_6)_2Pb$, as a plaster-like precipitate, soluble in alcohol.

1284. *Taurocholic acid*, $C_{26}H_{45}.NSO_7$, occurs in ox gall in only small quantity, and cannot be well extracted from it in a state of purity. To prepare it the solution of the salts from ox gall is first treated with normal plumbic acetate to precipitate glycocholic acid, and basic plumbic acetate then added to the filtrate to precipitate taurocholic acid. The latter precipitate is then washed, decomposed with sulphuretted hydrogen under water, and the solution evaporated.

The crystallised salts from dog's bile form a better crude material, as they contain only traces of glycocholic acid. The aqueous solution is first mixed with an amount of basic lead acetate by far insufficient for complete precipitation, and the filtrate precipitated with the same reagent. The last precipitate is then decomposed under water with sulphuretted hydrogen, the filtrate highly concentrated and mixed with ether; taurocholic acid then precipitates as a syrup that soon changes into needle-formed crystals. It is readily soluble in water and alcohol, its solutions being dextrorotary ($[\alpha] = + 24{\cdot}5°$), and is readily split up, either by boiling with pure water or more readily by acids and alkalies.

1285. *Cholic acid*, or *cholalic acid*, $C_{20}H_{40}O_5$, is the common decomposition product, together with glycocine or taurine, of both the acids previously mentioned, the splitting up being best effected by boiling for several days with baryta water:

$$C_{26}H_{43}NO_6 + H_2O = C_2H_5NO_2 + C_{24}H_{40}O_5,$$
$$C_{26}H_{45}NSO_7 + H_2O = C_2H_7NSO_3 + C_{24}H_{40}O_5.$$

The basic salt contained in the still hot liquid is decomposed by addition of hydrochloric acid, and the resulting amorphous precipitate, after washing with water, dissolved in a little sodic hydrate solution, and the liquid, after addition of some ether, again supersaturated with hydrochloric acid. The separated acid is dissolved in warm alcohol, and this mixed with water until turbidity ensues; after some days the acid crystallises. The crystals are either efflorescent tetragonal pyramids, containing five molecules of water, or prisms with one molecule of water which do not change in air. Cholic acid is readily soluble in alcohol and ether, difficultly in water. Its solutions are dextrorotary (+ 35°). Of the cholates those of the alkalies are readily soluble in water, baric cholate difficultly soluble, and plumbic cholate is insoluble in water, but soluble in boiling alcohol.

Free cholic acid and its salts give Pettenkofer's reaction very readily. On fusion with alkalies oils of aromatic odour are evolved, whilst the residuary saline mixture contains salts of volatile fatty acids, acetate, propionate, and butyrate.

1286. On boiling cholic acid with acids, or on heating it for a short time at 200°, it loses a molecule of water and is converted into

Cholodinic acid, $C_{24}H_{38}O_4$. It is a colourless, amorphous, resinous mass, insoluble in water, soluble in alcohol, which yields amorphous salts of bitter taste, soluble in alcohol. On longer boiling with acids or long heating at 200°, or more shortly at 300°, another molecule of water is eliminated and there remains

Dyslysine, $C_{24}H_{36}O_3$, a resin insoluble in water and alcohol, soluble in ether, which on long boiling with alcoholic potassic hydrate dissolves, being converted into potassic cholate. Dyslysine is soluble in concentrated sulphuric acid, and then gives Pettenkofer's reaction with a trace of sugar.

On long boiling of cholic acid with nitric acid, acetic, butyric, and higher fatty acids, together with nitroform, distil over, and the retort contains *choloidanic acid*, $C_{16}H_{24}O_7$, forming hair-like prisms nearly insoluble in cold water, together with oxalic acid and the dibasic *cholesterinic acid*, $C_8H_{10}O_5$, which forms a gummy mass.

1287. The acids derived from pig's bile differ essentially from the preceding; only very small quantities of the sulphurised acid are present together with considerable quantities of the sulphur-free acid.

Hyoglycocholic acid, $C_{27}H_{43}NO_5$, is amorphous and insoluble in water; its salts have a bitter taste.

Hyotaurocholic acid, $C_{27}H_{45}NSO_6$, has not been sufficiently investigated, as it only occurs in small quantity and is very readily decomposed.

On boiling with acids or alkalies they decompose into glycine or taurine and

Hyocholic acid, $C_{25}H_{40}O_4$, which can be obtained with difficulty in warty crystals, and is insoluble in water, but readily soluble in alcohol. On long boiling with acids it loses water and is converted into *hyodyslysine*, $C_{25}H_{38}O_3$.

The bile of the goose contains principally *chenotaurocholic acid*, $C_{29}H_{49}NSO_6$, homologous to hyotaurocholic acid. On boiling with baryta it is split up into taurine and *chenocholic acid*, $C_{27}H_{44}O_4$.

1288. *Lithofellic acid*, $C_{20}H_{36}O_4$, resembles the cholic acids in many respects, and gives Pettenkofer's reaction. It forms the chief constituent of certain Oriental bezoar stones (intestinal concretions of the Persian goat), from which it can be extracted with alcohol. It crystallises in small prisms, insoluble in water, and melts at 204°.

Cholesterine, $C_{26}H_{44}O$.

1289. Cholesterine is by no means a constituent of the bile only, but occurs in all cases where lecithin or its decomposition products exist, also in the protoplasma of animal and vegetable cells, in blood and many pathological liquids. It occurs especially richly in the brain, nerve substance, and yolk of eggs. The most convenient materials for its preparation are biliary calculi, which frequently consist of pure cholesterine. To obtain it perfectly pure it must be treated with alcoholic potash, in order to saponify any fats, and after washing recrystallised from hot alcohol, or better from a mixture of alcohol and ether.

Cholesterine forms large monoclinic prisms or tables of fatty feeling; the crystals contain one molecule of water, which is evolved at 100°. It is destitute of taste and odour, melts at 145°, and boils at about 360°, when air is excluded. It is quite insoluble in water, difficultly soluble in cold alcohol, readily in ether and acetic acid. Its solutions are lævorotary.

Cholesterine is a monacid alcohol, $C_{20}H_{43}.OH$, and as such is probably homologous with cinnamic alcohol (§ 1091). On heating with concentrated hydrochloric acid or phosphoric chloride it yields

Cholesteryl chloride, $C_{26}H_{43}Cl$, forming white needles soluble in alcohol. On heating with alcoholic ammonia it is converted into *cholesterylamide*, $C_{26}H_{43}NH_2$, forming colourless plates, melting at 104°. On heating cholesterine to 200° with organic acids, it yields crystalline salts, which are difficultly soluble in alcohol. *Cholesteryl acetate*, $C_{26}H_{43}.O.C_2H_3O$, melts at 92°. The butyrate, stearate, and benzoate have also been prepared. They are saponified by potash solution, again yielding cholesterine.

Like cinnamic alcohol, cholesterine also unites with two atoms of bromine, when solutions of the two in carbonic disulphide are mixed. On evaporation of the solvent cholesterine dibromide is left, in the form of small colourless needles; it melts at 147°, is difficultly soluble in alcohol, and on treatment with nascent hydrogen loses both atoms of bromine, cholesterine being regenerated.

Concentrated sulphuric acid on gentle heating resolves cholesterine into water and a mixture of colourless crystalline hydrocarbons of the formula $C_{26}H_{42}$, which are distinguished from one another by their fusing points and solubilities; they are partly isomeric with one another, but in part also polymers of that formula.

In this reaction an intense red colour is developed, especially at the commencement, which may be used in identifying cholesterine. On long boiling with nitric acid cholesterine is oxidised with formation of volatile fatty acids, which distil over with water vapour, whilst cholesteric acid is left in the retort, the reaction being similar to that with cholic acid.

Isocholesterine occurs together with cholesterine in that portion of the fatty matters in wool insoluble in alcohol. To separate them they are converted into benzoates by heating with benzoic acid, cholesteryl benzoate crystallising in thick plates, whilst isocholesteryl benzoate forms fine needles. On saponifying the benzoate with alcoholic potassic hydrate, isocholesterine is obtained in needles, melting at 137° and volatilising, apparently unchanged, at higher temperatures. Phosphoric pentachloride converts it into *isocholesteryl chloride:*

$$C_{26}H_{43}Cl.$$

Bile Pigments.

1290. The bile is always intensely coloured, sometimes green (especially with birds), sometimes greenish brown (ox gall), and finally bright yellow to deep brown (with pigs and human bile). This colouring proceeds mainly from two pigments—the green *biliverdin* and the red-brown *bilirubin.* Other pigments are found in small quantity in human biliary calculi.

All bile pigments contain nitrogen, are insoluble in water, soluble in aqueous alkalies, and when treated with nitrous acid give a series of colours, which are especially complete in the case of bilirubin, with which the yellowish red solution is coloured first green, then blue, violet, ruby red, and finally dirty yellow (Gmelin's colour reaction).

These colouring matters are most readily obtained from human biliary calculi. These are powdered, treated with ether alcohol until all cholesterine is removed, then treated with hydrochloric acid in order to decompose the calcium compound of the pigment contained in the calculi, then washed with water and dried. The resulting powder is extracted with chloroform as long as any colouring matter dissolves, and the filtered chloroform solution evaporated. The dark residue now yields *bilifuscin* to boiling alcohol, whilst the residual *bilirubin* is purified by solution in chloroform, precipitation by alcohol, and final recrystallisation from chloroform.

That portion originally insoluble in chloroform yields *biliprasin* to boiling alcohol; the residue, after renewed treatment with chloroform to remove the last traces of bilirubin, consists of *bilihumin.*

Biliverdin can only be prepared in a state of purity from bilirubin.

Bilirubin is, without doubt, a definite chemical compound, as also is biliverdin; biliprasin and bilifuscin, on the contrary, are not sufficiently well characterised as such. Bilihumin is certainly a mixture.

1291. 1. *Bilirubin,* $C_{16}H_{18}N_2O_3$, crystallises from chloroform in brownish red tables, little soluble in alcohol and ether, more readily in chloroform and benzene; it is also readily soluble in solutions of alkaline hydrates and of ammonia. The intensity of its colouring power is very great in solution; when only $\frac{1}{500000}$ is present a layer 1·5 c.m. thick is still distinctly yellow. The ammoniacal solution gives dark brown amorphous precipitates with calcic chloride, plumbic acetate, and other metallic salts; in these compounds one hydrogen atom has been replaced by metal, e.g. $(C_{16}H_{17}N_2O_3)_2Ca$. On addition of sodium amalgam to an alkaline bilirubin solution the colour is considerably lightened; addition of hydrochloric acid then precipitates brown flocks of *hydro-bilirubin,* which appears to be identical with *urobilin,* the brown colouring matter of urine.

2. *Biliverdin,* $C_{16}H_{20}N_2O_5$. Alkaline solutions of bilirubin on exposure to air, especially on heating, absorb oxygen and acquire an

intense green colour. On supersaturating with hydrochloric acid, biliverdin is precipitated as a fine green mass; it is insoluble in chloroform, but soluble in alcohol. The formation of biliverdin is probably represented by the equation:

$$C_{16}H_{17}KN_2O_3 + H_2O + O = C_{16}H_{19}KN_2O_5.$$

3. *Bilifuscin*, $C_{16}H_{20}N_2O_4$, and *biliprasin*, $C_{16}H_{22}N_2O_5$, are described as nearly black, shining, brittle masses, insoluble in ether and chloroform, soluble in alcohol and alkalies.

PROTEIN SUBSTANCES

1292. Protein substances are widely disseminated in the animal and vegetable kingdoms; they are the compounds taking the principal part in the physiological changes occurring in the organism. In the animal body, especially in that of the higher animals, they form the main part of the tissues (hence the name, from πρωτεύω), but occur also in nearly all animal liquids. They are without exception amorphous, and all contain nitrogen in addition to carbon, hydrogen, and oxygen, in most cases sulphur also. Accurate formulæ have not yet been obtained for any of these bodies, but from the results obtained it is certain that their molecules are very large and of very complicated structure. In agreement with this they do not diffuse through membranes, and are readily decomposed by putrefaction or by heating with aqueous acids or alkalies. Amongst the products of these decompositions there occur regularly ammonia, and amide derivatives of organic nuclei, such as glycocine, leucine, aspartic acid, glutamic acid, and tyrosine. On dry distillation they yield methylamine and pryridine bases in addition to ammonia. On heating with manganic oxide and sulphuric acid they yield very numerous oxidation products, amongst which there occur several volatile fatty acids, from formic acid upwards, together with their aldehydes and nitrils, benzaldehyde, benzoic acid, &c. Those protein substances soluble in water have without exception an action on polarised light; they are all precipitated by tannic acid, nearly all by alcohol.

Gelatinous Tissues and Gelatines.

1293. The gelatinous tissues occur only in the animal organism and are invariably organised; they are, as such, insoluble in cold or warm water, but swell up slightly and then putrefy readily. Solutions of tannins render them incapable of putrefaction by converting them into *leather*. On long boiling with water they are converted into *gelatines*, whose hot solutions on cooling become converted into a homogeneous jelly. This jelly dries on exposure to air into an amorphous transparent or semitransparent brittle mass, which only swells up in cold water; they are not dissolved by alcohol. On long boiling of the aqueous solutions, more quickly by heating to temperatures of 150° and above, they lose the property of gelatinising on cooling. On evaporation they then yield a mass resembling gelatine in most properties, but readily dissolved by cold water.

From their properties two varieties of gelatine may be distinguished, chondrine and glutine, the tissues from which they are derived being respectively designated as *chondrogen* and *collagen*.

Chondrogen and Chondrin.

1294. Bone cartilage previous to ossification, and therefore also the bony structure of the animal fœtus, consists essentially of *chondrogen.* It is also found in the cornea of the eye, and in all permanent cartilage, &c. It is purified by treating the cartilage with cold water, dilute acids, alkalies, alcohol, and ether, and then appears, after drying, as a structureless semitransparent mass.

On boiling the cartilage of the ribs for 12–24 hours with much water, *chondrin* goes into solution and gelatinises on cooling, and is precipitated by addition of alcohol. It is lævorotary. Alkalies or ammonia readily and completely dissolve chondrin jelly; the solution then possesses an enormous optical activity : $[a] = - 552°$.

Addition of acetic acid or of traces of mineral acids precipitates dissolved chondrin, but a very slight excess of the latter redissolves it. Chondrin behaves similarly with alum solution. It is precipitated completely by chlorine water, plumbic acetate, and argentic nitrate, only incompletely by mercuric chloride.

Boiling hydrochloric acid or gastric juice at blood heat decompose chondrin into a nitrogenous substance, which still requires examination, and a lævorotary substance, which reduces alkaline copper solutions. On boiling with sulphuric acid much leucine is formed, but no glycine.

After subtraction of the ash left on combustion, chondrin contains 50 % C, 6·6 % H, 14·4 % N, 0·4 % S, and 28·6 % O.

The gelatinous substance from the vertebræ of fish behaves similarly to chondrin except that it does not gelatinise.

Collagen and Glutine or Gelatine.

1295. *Collagen,* the substance yielding gelatine, forms the hyaline intracellular mass of the connective tissues, of the skin, sinews, &c., and also the organic portion of bones. On boiling with water, ossein dissolves more readily than chondrogen, being converted into *glutine,* which in the dry state forms glue, when in a state of greater purity is termed gelatine. The latter is chiefly prepared from the swimming bladder of fishes (sturgeon). A hot aqueous solution containing only one per cent. of glutine still gelatinises on cooling.

Glutine is readily dissolved by acids, including acetic, forming liquid glue; aqueous alkalies also dissolve it. Unlike chondrin, glutine solutions are not precipitated by normal or basic plumbic acetate, but are completely by mercuric chloride and also by tannic acid.

Glutine is also lævorotary: $[a] = - 130°$ at 30° temperature. On decomposition with dilute acids it yields glycocine and leucine. Whilst containing nearly an equal amount of carbon and hydrogen to chondrin, glutine contains essentially more nitrogen (18·3 %), the oxygen being correspondingly less.

1296. *Sericine,* or *silk gelatine,* may be included amongst these bodies, as it possesses the power of gelatinising in a very high degree; it is obtained from raw silk by long boiling with water. It is decomposed by boiling dilute sulphuric acid, with formation of a little leucine, about 5 % tyrosine and 10 % serine (§ 803).

ALBUMINOID SUBSTANCES.

1297. The albuminoids differ but little from one another in composition. After deducting ash they contain—

C = 50·6 — 54·3
H = 6·7 — 7·3
N = 12·8 — 18·4
S = ·4 — 1·7
O = 20·6 — 26·8.

Their formulæ must therefore be very complex, as from the percentages given above there must be to 1 atom of sulphur about 70 to over 300 atoms of carbon and about 110 to over 600 atoms of hydrogen. Only the true albumins are soluble as such in water, the others only being rendered soluble by aid of small quantities of acids, bases, or salts, with which they form transient compounds. In addition to these soluble modifications they can be converted in different ways into insoluble or 'coagulated' modifications. These latter are insoluble in water, and as a rule in salt solutions also; alkalies and acids redissolve them with difficulty. The conversion into the insoluble modification ensues either by heating, action of ferments, or long standing under strong alcohol, and appears to depend on the formation of more complicated molecules, accompanied by elimination of water. The action is therefore probably comparable to the formation of anhydride molecules from several simpler hydrated molecules. These anhydride coagulated molecules will then offer greater resistance to the solvent action of acids and alkalies, as they must be first hydrated and decomposed into the simpler molecules (hydrolysis).

Every albuminoid can be brought into solution by the action of alkalies or acids, especially of hydrochloric acid. The resulting alkali compounds are termed *albuminates*; the acid derivatives, *acid albumins* or *syntonins*. At first there is no permanent alteration effected by this means on the non-coagulated modifications, inasmuch as on neutralisation both the albuminates and acid albumins again yield the original albuminoid substance with unaltered properties.

On long continuance of the action, greater concentration of the reagents, and simultaneous action of heat (especially in the case of the coagulated albumins) decompositions readily ensue, in which all albumins yield leucine, tyrosine, and aspartic acid (the vegetable albumins also yielding glutamic acid), and invariably larger quantities of uncrystallisable compounds of unknown nature.

1298. These decompositions occur with especial ease on boiling with moderately dilute sulphuric acid, and also with solution of potassic hydrate. The relative yield of products, roughly determined, shows considerable variations. For instance, on heating with sulphuric acid (one part H_2SO_4 and four parts OH_2) there are obtained—

From	Leucine.	Tyrosine.	Aspartic Acid.	Glutamic Acid.
Egg albumin	10 %	1 %	Little or none.	
Myosin	18 %	1 %		
Fibrin	14 %	2 %		
Mucedine	4–12 %	None	?	2·5 %
Legumine		Little	3·5 %	1·5 %

On heating albuminoids with an equal quantity of bromine and ten times as much water in closed vessels, the formation of carbonic anhydride, bromoform, brom-acetic acid, oxalic acid, aspartic acid, leucine, and bromanil (§ 1006) is observed, there being obtained—

	Bromo-form.	Brom-acetic Acid.	Oxalic Acid.	Aspartic Acid.	Leucine.	Brom-anil.
Egg albumin .	30	22	12	23·8	22·6	1·5
Plant albumin	39	17	18·5	23·1	17·3	1·4
Casein . . .	37	22	11	9·3	19	·3
Legumine . .	45	26	12·5	14·5	18	1·4

The decomposition of albuminoids by solutions of alkalies yields similar products to those obtained with sulphuric acid. The formation of an alkaline sulphide is peculiar to them, so that the liquid evolves sulphuretted hydrogen on acidulation, and yields a black precipitate of plumbic sulphide on addition of a lead salt.

When moist the albuminoids putrefy with very great ease, probably in consequence of the presence of ferment-like organisms, with which as a matter of fact the putrefying mass swarms. There are then formed hydrogen, sulphuretted hydrogen, carbonic acid, ammonia, trimethylamine, ethylamine and its homologues, and in union with these members of the series of fatty acids, from acetic up to valeric acid, and also leucine and tyrosine.

On heating with much water to 150° all albuminoids, even the coagulated modifications, are converted into *readily soluble*, non-coagulable substances, without, however, suffering such decompositions as attend the action of acids and bases.

1299. The albuminoids show the following reactions, which are used for their identification:—

The aqueous saline, or very weakly acid or alkaline, solutions are precipitated in flocks by tannic acid and by salts of the heavy metals (e.g. lead, copper, mercury, &c.), and in most cases also by addition of alcohol.

Concentrated acetic acid and tribasic phosphoric acid dissolve all the albuminoids. The acetic solution after dilution is precipitated by potassic ferro- or ferricyanide or by potassic platino-cyanide.

Concentrated hydrochloric acid dissolves all albuminoids. On exposure to air, especially on boiling, this solution acquires a blue or bluish violet colour.

Strong nitric acid, especially that containing nitrous acid, colours them intensely *yellow*. The resulting nitro compounds dissolve in alkalies and ammonia with intensely reddish brown colour, and on addition of mineral acids to these salts are reprecipitated in flocks. These nitro products are known as *xanthoproteic acids*.

A solution of nitrate of mercury containing nitrous acid (Millon's reagent, formed by dissolving 1 part of mercury in 1 part of cold nitric acid, and afterwards diluting with 2 parts of water) gives a fine red colour with albuminoids, probably from the formation of mercury xanthoproteïnate.

On passing chlorine gas into solutions of the albuminoids, white flocculent precipitates are formed of chlor substitution products, containing from 6·5 % to 14 % of chlorine, according to the duration of the action. These dissolve in aqueous ammonia with formation of ammonic chloride and of albuminoid derivatives richer in oxygen, but still little investigated; they are termed *oxyproteïns.*

Concentrated sulphuric acid dissolves the albuminoids in the cold; on adding a little sugar (especially on exposure to air) a coloration ensues, at first red, then violet, resembling Pettenkofer's reaction for the bile acids (§ 1282).

They change the colour of Fehling's solution (§ 870) from blue to violet.

On heating in air they soften, then swell up and carbonise, emitting the disagreeable odour of burning feathers or hair; the charcoal formed is difficult to burn, and as a rule leaves an ash rich in calcic phosphate.

In general they show all the properties of the proteïn substances.

1300. Albuminoids suffer a peculiar change when exposed to the action of gastric juice; they dissolve in it at blood heat more or less quickly, being first converted into acid albumins, later into *peptones.* These peptones are soluble in water, are precipitated by addition of much strong alcohol, but not by addition of acids, alkalies, or acetic acid and potassic ferrocyanide; they are not converted into coagulated modifications, and, unlike the albuminoids, are highly diffusible. The peptones, therefore, appear to closely resemble the products of the action of a temperature of 150° on albuminoids and water, and are the forms in which the albuminoids of the food occur in the circulating juices of the animal body.

Albumins.

1301. Albumins occur dissolved in all animal or vegetable juices, and on heating the natural solutions are converted into the coagulated modifications, forming flocculent deposits from dilute solutions, whilst concentrated liquids solidify to a white opaque elastic mass, such as the white of eggs. The temperature of coagulation lies at 70°–73°.

Albumin solutions are not precipitated by addition of small quantities of dilute acids, alkaline carbonates, sodic chloride, or other alkaline salts in not too concentrated solution, whilst soluble salts of the heavy metals generally produce precipitates. Concentrated hydrochloric acid produces a precipitate, dissolving again in large excess with formation of acid albumins, a violet colour soon appearing. Strong nitric and metaphosphoric acids also precipitate the albumins, whilst acetic acid and tribasic phosphoric acid do not.

Alcohol precipitates the natural albumins; if the liquid is poured off quickly, the precipitate can be redissolved in pure water, whilst long contact with alcohol leads to the formation of the coagulated modifications.

Concentrated solutions of the alkaline hydrates convert strong albumin solutions into stiff jellys of alkali albuminates, which are soluble in pure water. The acid and alkali albuminates no longer contain unaltered albumins, as they are precipitated on neutralisation.

1302. *Egg albumin*, as a concentrated solution, forms the white of birds' eggs. From this it can be prepared by dilution with much water and filtration, when a nearly clear solution is obtained, which on evaporation at temperatures below 50° yields a yellowish transparent brittle mass, of sp. gr. 1·314. Some fat can be extracted from this by treatment with ether. In water it first swells up and then dissolves to a clear liquid. The specific rotary power of aqueous solution of egg albumin for yellow light is − 35·5°. The precipitate formed by strong nitric acid is either difficultly soluble or insoluble in excess. Ether precipitates concentrated solutions of egg albumin.

1303. *Serum albumin* occurs in all the liquids of the animal body, but is best obtained from the serum of blood, by dilution with twenty times its volume of water, precipitation of the globulin by passing carbonic anhydride, and evaporation of the filtrate below 50°. It closely resembles egg albumin, but possesses a different rotary power for yellow light = − 56°. Ether does *not* coagulate its solutions. The precipitates formed by nitric or hydrochloric acid dissolve much more readily in excess of acid than is the case with egg albumin.

The elementary composition of both varieties of albumin shows but little difference.

	C	H	N	S	O
Egg albumin . . .	53·4	7·0	15·6	1·6	22·4
Serum albumin . .	53·0	7·1	15·6	1·2	23·1

From these values the formula $C_{72}H_{112}N_{18}SO_{22}$ is derivable, but must be received with great caution. The composition of the artificially prepared potassic albuminate corresponds to the above formula + 2KOH.

1304. *Vegetable albumin* occurs in all vegetable juices, mostly in only small quantity; it has not yet been obtained in a state of purity in the soluble condition, but it shows the general properties of the albumins. It differs in composition from egg albumin in the amount of nitrogen (15·49–17·6 %, according to the source) and the less amount of sulphur (·76–1·55 %).

Globulins.

1305. The globulins resemble the albumins in the coagulability of their saline solutions on boiling, but differ from them very essentially in that they are insoluble in pure water though soluble in water containing 1–10 % of sodic chloride. Dilute acids readily convert them into syntonins (even 1 part of acid per 1,000 being sufficient), whilst very dilute alkalies dissolve them similarly to alkali albuminates, the coagulated modifications, however, being very difficultly soluble, and insoluble in common salt.

The acid globulins are separated from their solutions by addition of concentrated hydrochloric acid or of strong salt solutions. Their specific rotary power is very considerable, − 72° in the case of myosin-syntonin.

1306. *Vitellin.*—The yolk of birds' eggs consists of a concentrated solution of vitellin, together with *lutëin* (a yellow pigment which is soluble in ether and crystallisable), lecithine, some salts, and much fat. A very similar substance to vitellin occurs in the crystalline lense of the eye. To obtain vitellin the yolk of eggs is shaken with fresh quantities of ether until this latter no longer acquires any colour; the residue is then dissolved in a solution of common salt (1 %), the liquid filtered, and the vitellin precipitated by a large addition of water. Vitellin is coagulated on heating (at about 70°) by addition of alcohol, or of strong acids, but is not precipitated by addition of lead or copper salts to its sodic chloride solution, nor is it precipitated by saturation of its solution with sodic chloride.

1307. *Myosin* forms the chief constituent of the muscle plasma enclosed in the sarcolemma tubes of muscular fibre. In the living muscle it occurs in the liquid state, curdles partially and transitorily at every muscular contraction, completely shortly after death, when the *rigor mortis* sets in. This curdling is not a true coagulation. To prepare myosin, finely divided flesh is extracted with a ten per cent. solution of sodic chloride, and the filtered slimy liquid precipitated by saturation with common salt (distinction from vitellin). The flocculent precipitate is then collected, washed with a saturated solution of common salt, and finally dissolved by addition of such a quantity of water that a 10 % solution of common salt results. It is precipitated by large dilution with water, but with more difficulty than in the case of vitellin. It is quickly coagulated by heating with water or by addition of alcohol.

1308. *Globulin of the Blood and of the Serous Liquids.*—Globulin occurs, together with albumin and albuminates, in the chyle, in lymph, in blood and all serous liquids; in many of these liquids it occurs in large quantity, and these coagulate when no longer in contact with living tissues, with formation of fibrin, probably from the union of two different modifications of globulin—*fibrinogen* and *fibrinoplastic substances*—that which was originally in excess then remaining partly in solution.

The fibrinogen substance (frequently spoken of as *globulin*) occurs in all serous liquids (pericardial liquid, hydrocele, &c.), the fibrinoplastic substance, or *paraglobulin*, in blood serum (the liquid remaining after the fibrin and blood corpuscles have been separated from blood), in the aqueous humor of the eye, &c.

To prepare globulin, the respective liquids are mixed with about twenty times their volume of pure water, and carbonic acid then passed for a long time through the liquid. The globulin separates in flocks, which are dissolved to a clear liquid by a 1–10 % solution of sodic chloride. On mixing solutions of the two varieties together, fibrin is formed and separates. The whole difference between the two modifications is that paraglobulin is rather more readily precipitated from its dilute solutions, and easily loses the power of giving fibrin with globulin. The latter only loses its power of uniting with paraglobulin very slowly at ordinary temperatures, scarcely until putrefaction commences.

1309. *Fibrin* is the product of the action on one another (union) of the two globulins just mentioned. It commences as soon as their common solutions are out of contact with living tissue. The precipitation of fibrin can, however, be hindered by certain salts, such as Glauber's salts, or by reduction of the temperature to 0°; on the other hand, it may be accelerated by violent agitation of the solutions.

If the blood just freshly drawn from an artery is mixed with $\frac{1}{7}$ of its volume of sodic sulphate, and allowed to stand quietly, the blood corpuscles form a red deposit at the bottom, and a clear yellow-coloured liquid is left—a solution of blood plasma with sodic sulphate.

On largely diluting, fibrin separates. Pure blood plasma is best obtained from horse's blood. This is quickly cooled to 0°, and allowed to stand about one hour at this temperature; after the blood corpuscles have settled, the supernatant clear yellow plasma is poured off. At a few degrees above 0° it coagulates to a thin jelly, which soon shrinks together, whilst serum separates. This behaviour is also shown by the blood of all the higher animals still containing the blood corpuscles in suspension, but the separated fibrin carries the blood corpuscles with it, and so forms the red *blood-clots.*

Coagulated fibrin can readily be obtained pure by vigorous whipping of fresh blood with a bundle of twigs; it then separates in a fibrous state, and can be freed from the blood corpuscles by long-continued kneading under water.

These fresh white and elastic flocks of fibrin are very quickly digested by the gastric juice; they swell up in very dilute hydrochloric acid (1:1000), or in not too dilute solutions of sodic chloride, potassic nitrate, and other alkali salts, forming a shiny, jelly-like mass. The flocks shrink in concentrated hydrochloric acid, and only dissolve later with violet coloration. Oxygen is readily absorbed by fresh fibrin, carbonic anhydride being evolved and putrefaction soon ensuing; hydric peroxide is energetically decomposed with rapid evolution of oxygen.

Strong alcohol on heating completely coagulates fibrin, which contracts, and in the dry state forms a horn-like mass, which no longer shows the above properties.

1310. After subtraction of the ash the globulins have the following composition:—

	C	H	N	S	O
Vitellin . .	52·8	7·3	16·4	1·2	22·3
Myosin . . .	53·4	7·1	15·3	1·2	23·0
Blood fibrin .	52·6	7·0	17·4	1·2	21·8

Natural Alkali Albuminates.

1311. *Caseïn* only occurs largely in the milk of the mammalia, in slight quantity in yolk of eggs, in blood and other animal liquids. It is insoluble *per se*, occurring in these liquids as an alkali albuminate, and is precipitated on neutralising the alkali by dilute acid (as in the curdling of milk by the formation of lactic acid) or by the fermentive action of rennet, the dried inner stomach of the calf. These precipitations are only quite complete in the absence of phosphates of the alkalies. It is precipitated as albuminate by addition of readily soluble salts, e.g. magnesic sulphate, as also by cold alcohol. It is somewhat soluble in boiling alcohol.

To prepare it milk is largely diluted with water, and very dilute acetic acid added as long as a flocculent precipitate is formed. This latter carries the butter globules down with it, and therefore after washing with water requires treating with ether and alcohol to free it from fat. It is then dissolved in very dilute solution of sodic hydrate, and the clear solution precipitated anew by acetic acid.

When fresh, caseïn is very readily soluble in very dilute alkalies or mineral acids, forming albuminates or syntonins. On pouring the alkaline solutions into concentrated mineral acids, the acid caseïn separates in flocks, which are soluble in pure water.

On dissolving caseïn in strong solution of potash, the formation of potassic sulphide is soon observed.

The conversion into the true coagulated modification occurs on boiling milk, on the surface where in contact with air, and by heating the alkali solution to 50° with rennet. In composition caseïn closely approaches albumin.

1312. *Vegetable Caseïns.*—1. *Legumin* occurs as alkali albuminate in leguminosæ. Softened peas or beans are rubbed to a pulp, this stirred with much water, and all solid matters allowed to settle. The supernatant liquid, which is rendered turbid by fat, is cleared by filtration and precipitated by dilute acetic acid. The flocculent precipitate is collected and washed with ether and alcohol.

Legumin resembles caseïn; it dissolves in dilute acids and alkalies, and the albuminate solution on heating forms a pellicle-like milk.

2. *Conglutin* is the alkali albuminate of the sweet and bitter almonds, the kernels of stone fruit, and the lupins. It is prepared similarly to legumin, from which it only differs in elementary composition.

3. *Gluten caseïn* occurs, together with other proteïn substances, in most cereals and in the meal prepared from them. To obtain it flour is kneaded in a linen bag in constantly renewed water, until the latter is no longer rendered turbid by starch passing through; there is then left a grey, sticky, tenacious mass, termed *gluten;* it is a mixture of at least four different proteïn substances. 100 grams of this substance is extracted with a solution of 4 grams of potassic hydrate in 4 litres of water, the liquid allowed to stand several days separated from deposited matters, and acidulated with acetic acid. The separated mass is then successively treated at ordinary temperatures with alcohol of 60 % and 80 %, then with absolute alcohol, and finally with ether, and the residual gluten caseïn dried in vacuo.

Gluten caseïn is insoluble in water and alcohol, readily in dilute acids and alkalies, and also somewhat soluble in alcohol in the presence of acetic or tartaric acids. On boiling with water it is transformed into its coagulated modification.

1313. In addition *paralbumin* may be mentioned, which causes the slimy nature of the liquid of ovarian cysts. On diluting this largely, and passing carbonic anhydride through the liquid, or addition of acetic acid, a flocculent precipitate is obtained which readily dissolves in excess of acids and alkalies. Alcohol precipitates it as a flocculo-granular mass, which redissolves in water at 35° to a slimy viscous liquid.

1314. The elementary analysis of these five substances occurring naturally as albuminates gives the following percentage composition:—

	C	H	N	S	O
Milk caseïn . .	53·6	7·1	15·7	1·0	22·6
Legumin . . .	51·5	7·0	16·8	·4	24·3
Conglutin . . .	50·8	6·7	18·4	·4	23·7
Gluten caseïn .	51·0	6·7	16·1	·8	25·4
Paralbumin . .	51·8	6·9	12·8	1·7	26·8

1315. *Gluten fibrin, mucedin,* and *gliadin* are the constituents of gluten soluble in alcohol. For the preparation of these substances the alcoholic extract from the preparation of *gluten caseïn* is employed (§ 1312, 3). One-half of the alcohol is distilled off; on cooling *gluten fibrin* separates, is washed with absolute alcohol and ether, and redissolved in boiling 60 % alcohol. The hot filtered liquid on cooling deposits gluten fibrin as a tough, brownish yellow mass, becoming horn-like on drying; it is readily soluble in dilute alkalies and acids, and swells up in ammonia solution to a transparent jelly. It coagulates in boiling water, and is then no longer soluble in alcohol, dilute alkalies, or acids.

The alcoholic mother liquid from the preparation of gluten fibrin yields a varnish-like residue on evaporation; with the exception of a little gluten caseïn, this is soluble in 60–70 % cold alcohol; on adding 90 % alcohol to the filtrate flocks of *mucedin* separate, which are readily soluble in dilute acids and alkalies, and do not swell in water.

The strong alcoholic mother liquid contains *gliadin* (vegetable gelatine), which is left on evaporation as a tenacious mass insoluble in water. These last-mentioned substances have the following percentage composition:—

	C	H	N	S	O
Gluten fibrin .	54·3	7·2	16·9	1·0	20·6
Mucedin . . .	54·1	6·9	16·6	·9	21·5
Gliadin . . .	52·6	7·0	18·0	·9	21·5

ALBUMINOID FERMENTS.

1316. Some substances characterised by their powerful fermentive action stand in very close relation to some of the albuminoids. These are, in plants, *diastase*, *emulsin*, and *myrosin*, and in the animal body *ptyalin*, *pepsine*, the ferments of the pancreatic and intestinal liquids.

All these substances are soluble in water and are precipitated by alcohol, and also by plumbic acetate (as lead compounds). They are not precipitated by boiling their aqueous solutions, but lose their activity as ferments. They have mostly not yet been obtained even in a state of approximate purity.

1317. *Emulsin*, or *synaptase*, occurs in the sweet and bitter almonds, and is extracted from the latter by digestion for several hours with water, the fats having been previously removed by pressure. The filtered liquid is first treated with acetic acid to remove conglutin, and the clear solution then precipitated by strong alcohol. After the precipitate has been washed several times with alcohol, it is dried over sulphuric acid in vacuo, and is then obtained as a white friable mass, which on combustion leaves a very considerable quantity of ash (20–36 %), consisting in great part of calcic phosphate. Completely dry emulsin can be heated to 100° without affecting its activity. It dissolves in great part in water, and can then convert very large quantities of amygdalin into sugar, hydrocyanic acid, and benzoic aldehyde, and similarly of salicin into sugar and saligenin. Aqueous solution of emulsin readily decomposes with formation of much lactic acid. After subtracting the ash it contains in 100 parts: $C = 42·9$, $H = 7·1$, $N = 11·5$, $S = 1·2$, and $O = 37·3$.

1318. *Diastase*, or *maltin*, is the ferment formed from the gluten constituents of cereals during germination; it converts starch into dextrin and maltose. It is obtained from the aqueous extract of freshly germinated barley, by heating to 75° to coagulate albumin and then precipitating the diastase by strong alcohol. The aqueous solution readily decomposes with formation of acids. In a fresh state it possesses a most powerful fermentive action, one part of diastase transforming 100,000 parts of starch suspended in water. This action occurs most rapidly between 70° and 75°, but is totally and permanently lost at 100°.

1319. *Myrosin* is the ferment of mustard seeds, by which myronic acid is decomposed into sugar, sulphuric acid, and mustard oil (§ 1219).

1320. *Pepsin* is contained in the acid gastric juice secreted in the glands of the stomach, and can be separated from the other constituents by diffusion, as it will not pass through membranes. It is precipitated by strong alcohol or plumbic acetate, and also, though probably only mechanically, when calcic phosphate or cholesterine are precipitated from its solutions. In presence of acids—especially of hydrochloric acid—it converts all the albuminoids, even the coagulated, in very large quantity first into syntonins and then into peptones. It acts most quickly at about 40° (blood heat). It is scarcely altered by putrefaction.

1321. Ferments which convert starch into sugar are contained in the animal body in saliva (ptyalin), in the pancreatic secretion (pancreatin), in the liver, &c. On adding phosphoric acid and afterwards lime water to these liquids, the ferments are carried down with the precipitated calcic phosphate; this is dissolved in dilute acids, and then the ferment precipitated in flocks on addition of strong alcohol; these are soluble in pure water. They have been but little investigated.

PROTEIDS.

1322. The term proteids is applied to several substances occurring in the animal body in an insoluble state, and which have been derived from the albuminoids and in their chemical nature stand very near to the albumins. They possess the general proteïn reactions, are converted into xanthoproteic acids, with yellow coloration, by nitric acid, mostly give a rose-red coloration with Millon's reagent, and on treatment with concentrated acids and alkalies are converted slowly into compounds of acid albumin or albuminate-like character. On boiling with moderately concentrated sulphuric acid, or with strong alkalies, by dry distillation and long heating with water at 150°, they show in all essentials the behaviour of all proteïn compounds. Some of them are glucosides.

Animal Mucus.

1323. Animal mucus, or *mucin*, occurs in strongly swollen condition in different secretions, especially in bile, synovia, the saliva of the submaxillary gland, and as a glairy mucus on the mucous membranes of the respiratory passage and intestinal canal, &c. It is precipitated by alcohol or acetic acid from all these in a flocculent condition. It can be obtained in the state of greatest purity from the mucus of certain varieties of snails by rubbing the animals to pulp with sand, boiling with much water, and adding much acetic acid to the brown liquid. The separated mass is then washed with dilute acetic acid until the filtrate no longer gives a precipitate with a tannin solution, all salts removed by means of water, and the mass covered with dilute lime water. The mucine swells up in this, and for further purification is again precipitated by acetic acid. It remains unaltered under alcohol.

The mucous substances swell in water to an enormous extent, especially in the presence of certain alkali salts, yielding opalescent liquids. They are precipitated by alcohol, dilute mineral or organic acids, but are dissolved by free alkalies, or lime, or baryta water, as also by concentrated mineral acids. Neutral or alkaline liquids containing mucin are not precipitated by tannic acid, copper, mercury, or silver salts, nor by normal plumbic acetate, but are precipitated by basic plumbic acetate. On long boiling with dilute mineral acids they decompose into acid albumins, a substance resembling sugar and other substances. The mucins show rather varying compositions. 100 parts of mucin contain :—

C	H	N	O and S
48·9	6·8	8·5	35·8
52·2	7·0	12·6	28·2

Horny Tissues.

1324. *Elastin* occurs together with collagen in the connective tissue, in a state of special purity in the yellow *ligamentum nuchæ* of cattle. In consequence of its insolubility in alcohol, water, concentrated acetic acid, and boiling dilute hydrochloric acid and sodic hydrate, it is readily obtained pure. It forms a yellowish mass, very elastic in the moist condition, brittle when dry. On boiling with moderately concentrated sulphuric acid it yields much leucine (up to 50 %) and but little tyrosine.

1325. *Keratine*, the essential horn substance, forms the chief constituent of hair, feathers, nails, claws, horns, the epidermis and epithelium of the higher animals, and is freed from admixed substances similarly to elastin; it scarcely swells in water, more readily in strong acetic acid and solutions of alkaline hydrates. It dissolves in boiling acetic acid, also in strong alkalies, with formation of potassic sulphide. Boiling sulphuric acid decomposes it with formation of leucine (about 10 %) and proportionally much tyrosine (3–4 %).

1326. *Fibroïn* is contained in silk, and remains as a horny mass after the removal of the sericine (§ 1296); it is soluble in an ammoniacal solution of cupric oxide (comp. § 883). It is also soluble in concentrated acids and alkalies, the solutions giving tenacious precipitates on neutralisation. Decomposition with dilute sulphuric acid yields glycocine, leucine, and 5 % tyrosine.

1327. *Spongin*, the chief constituent of sponges, is left as an insoluble substance on treating these with ether, alcohol, water, hydrochloric acid, and dilute sodic hydrate; it contracts in ammoniacal solution of cupric oxide, and on decomposition with sulphuric acid yields leucine, but neither tyrosine nor glycocine.

1328. After subtracting the ash, the substances of this group show the following composition:—

<table>
<tr><th></th><th>C</th><th>H</th><th>N</th><th>S</th><th>O</th></tr>
<tr><td>Elastin . .</td><td>55·4</td><td>7·4</td><td>16·7</td><td colspan="2">20·5</td></tr>
<tr><td>Keratin .</td><td>50·3–52·5</td><td>6·4–7·0</td><td>16·2–17·7</td><td>·7–5</td><td>20·7–25·0</td></tr>
<tr><td>Fibroïn . .</td><td>48·8</td><td>6·2</td><td>19·0</td><td colspan="2">26·0</td></tr>
<tr><td>Spongin .</td><td>46·5</td><td>6·3</td><td>16·1</td><td colspan="2">31·1</td></tr>
</table>

1329. *Nucleïn* occurs in the nucleus of pus globules and in the blood corpuscles of snakes and birds. It can be readily isolated, as it is not digested by gastric juice at blood heat and is insoluble in water, alcohol, ether, and dilute alkalies and acids. It is only dissolved by concentrated alkalies or mineral acids, and even then only slowly. The freshly prepared hydrochloric acid solution is again precipitated by water.

Nucleïn contains 49·6 % C, 7·1 % H, 14–15 % N, 2 % S, about 2·3 % P, and 24–25 % O.

Amyloid matter occurs only pathologically in the form of concentric scaly granules in the serous coating of the brain and nerves, and as a waxy infiltration in the liver, spleen, and kidneys. The glands altered by such infiltrations are finely divided, are extracted with ether and alcohol, and finally digested with gastric juice at 40° in order to convert all albuminoids into peptones. The amyloid substance then remains unattached. Alkalies dissolve it with difficulty, converting it into albuminate; acids similarly convert it into acid albumin. It is characterised by the red coloration that it gives with iodine and the violet or blue colour with iodine and sulphuric acid. On analysis it gives the following percentages:—

53·6 C, 7·0 H, 15·0 N, and 24·4 O and S (S being about 1·3).

HÆMOGLOBINS.

1330. The blood pigments, or hæmoglobins, occupy a peculiar position amongst the proteïn substances. They form the chief constituent of the red blood corpuscles of the vertebratæ, and occur dissolved in the muscle of the mammalia and the blood of some of the invertebratæ, e.g. in log worms. In a state of purity all hæmoglobins appear to be crystalline, but do not all crystallise equally well nor with equal readiness.

To prepare them the blood corpuscles must first be isolated as far as possible, which is best effected by the quiet standing for several days of a mixture of 1 volume of defibrinated blood with 10 volumes of a three per cent. sodic chloride solution. The red corpuscles then deposit so completely that the liquid can be poured off them. The red mud is then brought into a flask by means of water, and well shaken after addition of an equal volume of ether. The hæmoglobin is dissolved; the solution is filtered as quickly as possible, cooled to 0°, and the hæmoglobin precipitated in crystals by addition of $\frac{1}{4}$ volume of alcohol. The colouring matters of the blood of the dog, rat, hippopotamus, and rhinoceros crystallise as a rule before the addition of the alcohol; that from the blood of birds crystallises with more difficulty after the addition of alcohol; whilst most difficulty is experienced in inducing the crystallisation of the hæmoglobin of horse or human blood. Hæmoglobin can be recrystallised by dissolving in water at 40°, quickly filtering, cooling to 0°, and adding alcohol.

1331. All hæmoglobins are of a blood red or brick red colour when in powder; they contain iron and water of crystallisation, and do not quite agree with one another in their quantitative composition. For instance, 100 parts of dried hæmoglobin crystals contain:—

	C	H	N	Fe	S	O
From the dog . . .	53·9	7·3	16·2	·4	·4	21·8
„ rhinoceros .	54·1	7·4	16·1	·6	·4	21·4

the first containing 3–4 % of water of crystallisation, the latter 9–5 %.

The crystalline forms are very different.

The blood of the hippopotamus and the rat yields rhombic tetrahedrons and octahedrons.

The blood of the rhinoceros gives hexagonal tables, whilst the blood of the goose gives rhombic tables.

All crystalline blood pigments are *oxyhæmoglobins*, i.e. loose compounds of true hæmoglobins with oxygen, which latter they give off in vacuo—especially on gently heating the solution—and reabsorb on exposure to air. The loosely united oxygen of the oxyhæmoglobins can also be readily removed by easily oxidisable substances—such as ferrous or stannous tartrates—with reduction to hæmoglobin. Reduced hæmoglobin and oxyhæmoglobin solutions are characterised by their absorption spectra; that of the latter shows two distinct absorption bands, one in the yellow, the other in the green—both between Fraunhofer's D and E lines, and separated by a band of yellowish green light. The absorption spectrum of the hæmoglobin shows, on the contrary, only a single broad band, thinning out at the edges, and whose darkest part covers the clear interspace between the bands of oxyhæmoglobin.

Hæmoglobin also unites with nitric oxide and carbonic oxide gas to form relatively very stable crystalline compounds.

Whilst perfectly dry oxyhæmoglobin can be heated to 100° without alteration, that containing water, especially when in solution, decomposes at about 70° in coagulated albumin and *hæmatin*, a pigment containing iron. The same decomposition is effected by the action of alkalies or acids.

1332. *Hæmatin*, $C_{34}H_{34}N_4FeO_5$, is usually obtained in the form of a salt from the decomposition of oxyhæmoglobin by acids, &c.

Hæmatin hydrochloride, or *hæmin*, is readily obtained from defibrinated blood by evaporating the hæmoglobin solution prepared from the deposited red corpuscles in shallow vessels over sulphuric acid, and heating the resulting syrup for some hours on the water bath with 10–20 times its volume of glacial acetic acid. The liquid, which contains the albumin in solution as acid albumin, on dilution yields hæmatin hydrochloride in the form of a black crystalline powder of metallic lustre, which dissolves readily in water containing a little alkali to a brown dichroic liquid. It contains 5·2 % chlorine, i.e. one atom to the above hæmatin formula.

The formation of microscopic crystals of hæmin affords a useful test for the presence of blood in medico-legal cases. For this purpose only a very small portion of the dried blood is requisite; it is placed together with a little common salt on an object glass, a cover glass placed over it, and the interspace between the two filled with glacial acetic acid. Heat is then applied until bubbles appear in the acetic acid, and then on cooling the liquid is full of numerous reddish brown to black microscopic hæmin crystals, which as a rule show the form of rhombic tables.

On boiling the blood corpuscle deposit with alcoholic sulphuric acid, *hæmatin sulphate* is formed and crystallises on cooling.

Hæmatin is obtained from both salts by dissolving in dilute solution of potassic hydrate and neutralising with acetic acid, when it is precipitated in the amorphous condition, and after drying forms a bluish black mass of metallic lustre, which yields a brownish black powder. It is insoluble in water, difficultly soluble in alcohol, somewhat in acetic acid, and readily soluble in alkalies.

Hæmatin corresponds to oxyhæmoglobin. From reduced hæmoglobin another pigment is obtained, which is converted into hæmatin on oxidation.

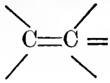
1333. The other animal colouring matters stand without doubt in close relationship to hæmatin. Hæmatoidin, obtained by the decomposition of old blood extravasations, e.g. in the brain, does not contain iron and appears to be identical with bilirubin, or more probably with *luteïn*, the colouring matter of the yolk of eggs. *Melanine*, the black pigment of the choroid, skin, hair, &c., as also *urobilin*, or hydrobilirubin, the normal colouring matter of urine, are probably also formed in the body from blood pigments.

APPENDIX.

I.—Refraction Equivalents of Organic Compounds.

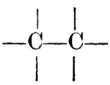
(Comp. p. 52.)

It has been shown lately by experiments on unsaturated compounds that the refraction equivalent of carbon is greater in those cases where double linking has taken place between two carbon atoms than is the case where the compound is saturated, or where, though unsaturated, there is still no multiple linking of carbon atoms. Each such case of double union appears to add about 2 to the refraction equivalent; so that the refraction equivalent of the group



$$= 2 \times 5 + 2 = 12{\cdot}0,$$

the saturated group



$$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-$$

being $2 \times 5 = 10{\cdot}0$.

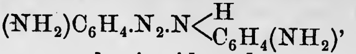
Oxygen has two values. Where united to a carbon atom by double linking it = 3·29, whilst in those cases where the oxygen is in union with two atoms of other elements the value is reduced to 2·71.

II.—The Diazo Colours.

Of late years a large number of compounds have been discovered containing the *diazo group* —N═N— (see p. 576); and as these are now of great technical importance on account of the brilliant shades of yellow, orange, and scarlet which they impart to various fabrics when used as dyes, it has been considered necessary to add this brief account of their preparation and properties.

The colouring matters belonging to the present class may be considered as being formed on the type of *amido-azobenzene* and '*Bismarck brown,*' which have already been mentioned (p. 578), but containing acid instead of basic radicals. Thus, when nitrous acid acts upon a cold alcoholic solution of aniline, diazoamido-benzene is formed, in accordance with the equation:

$$2C_6H_5.NH_2 + HNO_2 = C_6H_5.N_2.N{<}^{H}_{C_6H_5} + 2H_2O.$$

This diazoamido-benzene, when allowed to stand for some time in the presence of alcohol and an aniline salt, undergoes isomeric transformation into *amidoazo-benzene*, $C_6H_5.N_2.C_6H_4(NH_2)$, a substance of feeble tinctorial power long known as 'aniline yellow.' Similarly, when nitrous acid acts upon metadiamido-benzene, the first product is *diazodiamido-benzene*,  $(NH_2)C_6H_4.N_2.N<\begin{smallmatrix}H\\C_6H_4(NH_2)\end{smallmatrix}$, which changes into the isomeric compound *triamido-azobenzene*, or 'Bismarck brown,' $(NH_2)C_6H_4.N_2.C_6H_3(NH_2)_2$. It will be seen that this last compound as well as 'aniline yellow,' on which type the diazo colours are formed, consist of *two* aromatic nuclei having one or more hydrogen atoms replaced by an amido group and linked together by the diazo group.

A body intermediate between amido-azobenzene and triamido-azobenzene, viz. *diamido-azobenzene*, is formed by the action of diazobenzene chloride upon metadiamido-benzene:

$$C_6H_5.N_2.Cl + C_6H_4(NH_2)_2 = C_6H_5.N_2.C_6H_3(NH_2)_2 + HCl.$$

This colouring matter, known by the name of '*chrysoidine*,' is an orange dye and forms beautifully crystalline salts having a beetle-green metallic lustre.

The last reaction is typical of the formation of the diazo colours generally. Diazo compounds of benzene and its homologues are made to act upon the phenols and their sulphonic acids, primary and secondary monamines, &c. The first of these colours made on a large scale was an orange dye formed by the action of diazo-sulphanilic acid upon dimethyl aniline and having the constitution:

$$(HSO_3)C_6H_4.N_2.C_6H_4.N(CH_3)_2.$$

The value of these dyes is greatly increased by the presence of acid radicals, the most valuable and widely known of these colours being the various shades of scarlet produced by the action of diazo-xylene and diazo-cumene chloride upon the disulphonic acid of β-naphthol, and having therefore the constitution:

$$C_6H_3(CH_3)_2.N_2.C_{10}H_4(HO)(HSO_3)_2, \&c.$$

These colours are rapidly replacing cochineal, which they equal in brilliancy and fastness and greatly excel in tinctorial power.

By using the sulphonic acids of diazo-benzene and its homologues, and the disulphonic acid of β-naphthol, a series of diazo colours containing three HSO_3 groups is obtained, these also being various shades of orange and scarlet. These bodies have the constitution:

$$(HSO_3)C_6H_4.N_2.C_{10}H_4(HO)(HSO_3)_2;$$
$$(HSO_3)C_6H_2(CH_3)_2.N_2.C_{10}H_4(HO)(HSO_3)_2, \&c.$$

It is unnecessary to give here a detailed account of each of the diazo colours, as their general chemical history will be readily comprehended from the above-given typical examples. The bodies formed from diazo-benzene and its homologues and β-naphthol-disulphonic acid increase in redness as the homologous series is ascended. Thus diazo-benzene chloride gives an orange and diazo-cumene a bluish scarlet, these two extremes being connected by intermediate shades.

Another class of diazo colours has recently been discovered, having the constitution of *three* substituted aromatic nuclei linked together by two diazo groups. These compounds are formed by converting the amido group of amidoazo-benzene and its homologues (or their sulphonic acids) into a diazo group by the action of nitrous acid. To take a typical example :

$$\underset{\text{Amidoazo-benzene.}}{C_6H_5.N_2.C_6H_4(NH_2)} + HNO_2 + HCl$$

$$= \underset{\text{Diazoazo-benzene chloride.}}{C_6H_5.N_2.C_6H_4.N_2.Cl} + 2H_2O.$$

The diazo-azo compounds are then made to act upon the phenols or their sulphonic acids, when they give rise to the formation of colouring matters of various shades of scarlet and having the constitution $C_6H_5N_2.C_6H_4.N_2.C_{10}H_4(HO)(HSO_3)_2$, &c.

The colours of this group have a greater tinctorial power than have those previously treated.

INDEX.

VALUABLE BOOKS RELATING TO CHEMISTRY.

ARMSTRONG (Prof. H. E.) Introduction to the Study of Organic Chemistry. 12mo. Cloth, $1.50.

COOKE (Prof. JOSIAH PARSONS, Jr., of Harvard University). The New Chemistry. 12mo. Cloth, $2.00.

HOFFMANN, FREDERICK. Manual of Chemical Analysis, as applied to the Examination of Medicinal Chemicals. A Guide for the Determination of their Identity and Quality, and for the Detection of Impurities and Adulterations. For the Use of Pharmaceutists, Physicians, Druggists, and Manufacturing Chemists, and Students. Cloth, $3.00.

JOHNSTON (Prof. JAMES F. W.) The Chemistry of Common Life. A new edition, revised, enlarged, and brought down to the Present Time. By Arthur Herbert Church, M. A., Oxon., author of "Food: its Sources, Constituents, and Uses." Illustrated with Maps and numerous Engravings on Wood. 12mo. Cloth, $2.00.

MILLER (W. ALLEN). Introduction to the Study of Inorganic Chemistry. With 71 Figures on Wood. 12mo. Cloth, $1.50.

RAINS (GEORGE W., M. D.) Chemical Exercises in Qualitative Analysis, for Ordinary Schools. By George W. Rains, M. D., Professor of Chemistry and Pharmacy in the Medical Department of the University of Georgia, etc. Cloth, flexible, 50 cents.

ROSCOE and SCHORLEMMER. A Treatise on Chemistry. By H. E. Roscoe, F. R. S., and C. Schorlemmer, F. R. S., Professors of Chemistry in the Victoria University, Owens College, Manchester. With Illustrations.
Vols. I and II, 8vo. Inorganic Chemistry.
Vol. I. The Non-Metallic Elements. Containing a Portrait of Dutton, engraved by C. H. Jeens. Cloth, $5.00.
Vol. II. Metals. Two Parts. Cloth, $3.00 each.

STRECKER–WISLICENUS. Short Text-book of Organic Chemistry. Translated and edited, with extensive Additions, by W. R. Hodgkinson, Ph. D. (Würzburg), and A. J. Greenaway, F. I. C., F. C. S. Small 8vo.

THORPE and MUIR. Qualitative Chemical Analysis and Laboratory Practice. 12mo. Cloth, $1.50.

TILDEN (W. A., F. C. S.) Introduction to the Study of Chemical Philosophy. 12mo. Cloth, $1.50.

VOGEL (Dr. HERMANN). The Chemistry of Light and Photography. With 100 Illustrations. 12mo. Cloth, $2.00.

WAGNER, RUDOLF. Hand-book of Chemical Technology. Translated and edited from the eighth German edition, with extensive Additions, by William Crookes, F. R. S. With 336 Illustrations. 8vo. Cloth, $5.00.

YOUMANS (Prof. E. L.) Class-book of Chemistry. New edition. 12mo. Cloth, $1.50.

New York: D. APPLETON & CO., 1, 3, & 5 Bond Street.

RECENT ADDITIONS

TO THE

INTERNATIONAL SCIENTIFIC SERIES.

THE SUN. By C. A. Young, Ph. D., LL. D., Professor of Astronomy in the College of New Jersey. With numerous Illustrations. 12mo, cloth. $2.00.

"Professor Young is an authority on 'The Sun,' and writes from intimate knowledge. He has studied that great luminary all his life, invented and improved instruments for observing it, gone to all quarters of the world in search of the best places and opportunities to watch it, and has contributed important discoveries that have extended our knowledge of it.

"It would take a cyclopædia to represent all that has been done toward clearing up the solar mysteries. Professor Young has summarized the information, and presented it in a form completely available for general readers. There is no rhetoric in his book; he trusts the grandeur of his theme to kindle interest and impress the feelings. His statements are plain, direct, clear, and condensed, though ample enough for his purpose, and the substance of what is generally wanted will be found accurately given in his pages."—*Popular Science Monthly.*

VOLCANOES: What they Are and what they Teach. By J. W. Judd, Professor of Geology in the Royal School of Mines (London). With Ninety-six Illustrations. 12mo, cloth. $2.00.

"In no field has modern research been more fruitful than in that of which Professor Judd gives a popular account in the present volume. The great lines of dynamical, geological, and meteorological inquiry converge upon the grand problem of the interior constitution of the earth, and the vast influence of subterranean agencies. . . . His book is very far from being a mere dry description of volcanoes and their eruptions; it is rather a presentation of the terrestrial facts and laws with which volcanic phenomena are associated."—*Popular Science Monthly.*

"The volume before us is one of the pleasantest science manuals we have read for some time." —*Athenæum.*

"Mr. Judd's summary is so full and so concise, that it is almost impossible to give a fair idea in a short review."—*Pall Mall Gazette.*

ILLUSIONS: A Psychological Study. By James Sully, author of "Sensation and Intuition," etc. 12mo, cloth. $1.50.

This volume takes a wide survey of the field of error, embracing in its view not only the illusions commonly regarded as of the nature of mental aberrations or hallucinations, but also other illusions arising from that capacity for error which belongs essentially to rational human nature. The author has endeavored to keep to a strictly scientific treatment—that is to say, the description and classification of acknowledged errors, and the exposition of them by a reference to their psychical and physical conditions.

"An interesting contribution by Mr. James Sully to the study of mental pathology. The author's field of inquiry covers all the phenomena of illusion observed in sense-perception, in the introspection of the mind's own feelings, in the reading of others' feelings, in memory, and in belief. The author's conclusions are often illustrated by concrete example or anecdote, and his general treatment of the subject, while essentially scientific, is sufficiently clear and animated to attract the general reader."—*New York Sun.*

"This is not a technical work, but one of wide popular interest, in the principles and results of which every one is concerned. The illusions of perception of the senses and of dreams are first considered, and then the author passes to the illusions of introspection, errors of insight, illusions of memory, and illusions of belief. The work is a noteworthy contribution to the original progress of thought, and may be relied upon as representing the present state of knowledge on the important subject to which it is devoted."—*Popular Science Monthly.*

New York: D. APPLETON & CO., 1, 3, and 5 Bond Street.

SCIENTIFIC PUBLICATIONS.

General Physiology of Muscles and Nerves.

By Dr. I. Rosenthal, Professor of Physiology at the University of Erlangen. With seventy-five Woodcuts. ("International Scientific Series.") 12mo. Cloth, $1.50.

"The attempt at a connected account of the general physiology of muscles and nerves is, as far as I know, the first of its kind. The general data for this branch of science have been gained only within the past thirty years."—*Extract from Preface.*

Sight:

An Exposition of the Principles of Monocular and Binocular Vision. By Joseph Le Conte, LL. D., author of "Elements of Geology"; "Religion and Science"; and Professor of Geology and Natural History in the University of California. With numerous Illustrations. 12mo. Cloth, $1.50.

"It is pleasant to find an American book which can rank with the very best of foreign works on this subject. Professor Le Conte has long been known as an original investigator in this department; all that he gives us is treated with a master-hand."—*The Nation.*

Animal Life,

As affected by the Natural Conditions of Existence. By Karl Semper, Professor of the University of Würzburg. With two Maps and one hundred and six Woodcuts, and Index. 12mo. Cloth, $2.00.

"This is in many respects one of the most interesting contributions to zoölogical literature which has appeared for some time."—*Nature.*

The Atomic Theory.

By Ad. Wurtz, Membre de l'Institut; Doyen Honoraire de la Faculté de Médecine; Professeur à la Faculté des Sciences de Paris. Translated by E. Cleminshaw, M. A., F. C. S., F. I. C., Assistant Master at Sherborne School. 12mo. Cloth, $1.50.

"There was need for a book like this, which discusses the atomic theory both in its historic evolution and in its present form. And perhaps no man of this age could have been selected so able to perform the task in a masterly way as the illustrious French chemist, Adolph Wurtz. It is impossible to convey to the reader, in a notice like this, any adequate idea of the scope, lucid instructiveness, and scientific interest of Professor Wurtz's book. The modern problems of chemistry, which are commonly so obscure from imperfect exposition, are here made wonderfully clear and attractive."—*The Popular Science Monthly.*

The Crayfish.

An Introduction to the Study of Zoölogy. By Professor T. H. Huxley, F. R. S. With eighty-two Illustrations. 12mo. Cloth, $1.75.

"Whoever will follow these pages, crayfish in hand, and will try to verify for himself the statements which they contain, will find himself brought face to face with all the great zoölogical questions which excite so lively an interest at the present day."

"The reader of this valuable monograph will lay it down with a feeling of wonder at the amount and variety of matter which has been got out of so seemingly slight and unpretending a subject."—*Saturday Review.*

New York: D. APPLETON & CO., 1, 3, & 5 Bond Street.

SCIENTIFIC PUBLICATIONS.

The Human Species.

By A. De Quatrefages, Professor of Anthropology in the Museum of Natural History, Paris. 12mo. Cloth, $2.00.

The work treats of the unity, origin, antiquity, and original localization of the human species, peopling of the globe, acclimatization, primitive man, formation of the human races, fossil human races, present human races, and the physical and psychological characters of mankind.

Modern Chromatics.

With Applications to Art and Industry. With one hundred and thirty Original Illustrations, and Frontispiece in Colors. By Ogden N. Rood, Professor of Physics in Columbia College. 12mo. Cloth, $2.00.

"In this interesting book Professor Rood, who, as a distinguished Professor of Physics in Columbia College, United States, must be accepted as a competent authority on the branch of science of which he treats, deals briefly and succinctly with what may be termed the scientific *rationale* of his subject. But the chief value of his work is to be attributed to the fact that he is himself an accomplished artist as well as an authoritative expounder of science."—*Edinburgh Review*, *October*, 1879, *in an article on "The Philosophy of Color."*

Education as a Science.

By Alexander Bain, LL. D. 12mo. Cloth, $1.75.

"This work must be pronounced the most remarkable discussion of educational problems which has been published in our day. We do not hesitate to bespeak for it the widest circulation and the most earnest attention. It should be in the hands of every school-teacher and friend of education throughout the land."—*New York Sun.*

A History of the Growth of the Steam-Engine.

By Robert H. Thurston, A. M., C. E., Professor of Mechanical Engineering in the Stevens Institute of Technology, Hoboken, N. J., etc. With one hundred and sixty-three Illustrations, including fifteen Portraits. 12mo. Cloth, $2.50.

"Professor Thurston almost exhausts his subject; details of mechanism are followed by interesting biographies of the more important inventors. If, as is contended, the steam-engine is the most important physical agent in civilizing the world, its history is a desideratum, and the readers of the present work will agree that it could have a no more amusing and intelligent historian than our author."—*Boston Gazette.*

Studies in Spectrum Analysis.

By J. Norman Lockyer, F. R. S., Corespondent of the Institute of France, etc. With sixty Illustrations. 12mo. Cloth, $2.50.

"The study of spectrum analysis is one fraught with a peculiar fascination, and some of the author's experiments are exceedingly picturesque in their results. They are so lucidly described, too, that the reader keeps on, from page to page, never flagging in interest in the matter before him, nor putting down the book until the last page is reached."—*New York Evening Express.*

New York: D. APPLETON & CO., 1, 3, & 5 Bond Street.

SCIENTIFIC PUBLICATIONS.

Text-book of Systematic Mineralogy.

By Henry Bauerman, F. G. S., Associate of the Royal School of Mines. (New volume in the "Text-books of Science Series.") 16mo. Cloth, $2.50.

Anthropology:

An Introduction to the Study of Man and Civilization. By Edward B. Tylor, D. C. L., F. R. S., author of "Primitive Culture," "The Early History of Mankind," etc. With seventy-eight Illustrations. 12mo. With Index. Cloth, $2.00.

"Mr. Tylor's admirable little book certainly deserves the success with which it will doubtless meet."—*Pall Mall Gazette.*

Scientific Culture, and other Essays.

By Joseph Parsons Cooke, Professor of Chemistry and Mineralogy in Harvard College. One vol., square 16mo. Cloth, $1.00.

Popular Lectures on Scientific Subjects.

By H. Helmholtz, Professor of Physics at the University of Berlin. Second Series. 12mo. Cloth, $1.50.

The favor with which the first series of Professor Helmholtz's lectures was received justifies, if a justification is needed, the publication of the present volume.

The Power of Movement in Plants.

By Charles Darwin, LL. D., F. R. S., assisted by Francis Darwin. With Illustrations. 12mo. Cloth, $2.00.

"Mr. Darwin's latest study of plant-life shows no abatement of his power of work or his habits of fresh and original observation. We have learned to expect from him at intervals, never much prolonged, the results of special research in some by-path or other subordinated to the main course of the biological system associated with his name; and it has been an unfailing source of interest to see the central ideas of the evolution and the continuity of life developed in detail through a series of special treatises, each wellnigh exhaustive of the materials available for its subject."—*Saturday Review.*

A Physical Treatise on Electricity and Magnetism.

By J. E. H. Gordon, B. A., Assistant Secretary of the British Association. With about two hundred full-page and other Illustrations. Two vols., 8vo. Cloth, $7.00.

"We welcome most heartily Mr. Gordon's valuable contribution to the experimental side of the science. It at once takes its place among the books with which every investigator and every teacher who goes beyond the merest rudiments must needs equip himself. There is certainly no book in English—we think there is none in any other language—which covers quite the same ground. It records the most recent advances in the experimental treatment of electrical problems, it describes with minute carefulness the instruments and methods in use in physical laboratories, and is prodigal of beautifully executed diagrams and drawings made to scale."—*London Times.*

New York: D. APPLETON & CO., 1, 3, & 5 Bond Street.

Books for Every Household.

Cooley's Cyclopædia of Practical Receipts,

And Collateral Information in the Arts, Manufactures, Professions, and Trades, including Medicine, Pharmacy, and Domestic Economy. Designed as a Comprehensive Supplement to the Pharmacopœia, and General Book of Reference for the Manufacturer, Tradesman, Amateur, and Heads of Families. *Sixth edition.* Revised and partly rewritten by Richard V. Tuson, Professor of Chemistry and Toxicology in the Royal Veterinary College. Complete in two volumes, 8vo, 1,796 pages. With Illustrations. Price, $9.00.

"The great characteristic of this work is its general usefulness. In covering such diverse subjects, the very best and most recent research seems to have been sought for, and the work is remarkable for intelligent industry. This very complete work can, then, be highly recommended as fulfilling to the letter what it purports to be—a cyclopædia of practical receipts."—*New York Times.*

"It is a well-edited special work, compiled with excellent judgment for special purposes, which are kept constantly in mind. If it is more comprehensive than its title suggests, that is only because it is impossible to define the limits of its purpose with exactitude, or to describe its contents upon a title-page. Illustrations of the text are freely used, and the mechanical execution of the work is excellent."—*New York Evening Post.*

The Chemistry of Common Life.

By the late Professor James F. W. Johnston. A new edition, revised and enlarged, and brought down to the Present Time, by Arthur Herbert Church, M. A., Oxon., author of "Food: its Sources, Constituents, and Uses." Illustrated with Maps and numerous Engravings on Wood. In one vol., 12mo, 592 pages. Cloth, price, $2.00.

Summary of Contents.—The Air we Breathe; the Water we Drink; the Soil we Cultivate; the Plant we Rear; the Bread we Eat; the Beef we Cook; the Beverages we Infuse; the Sweets we Extract; the Liquors we Ferment; the Narcotics we Indulge in; the Poisons we Select; the Odors we Enjoy; the Smells we Dislike; the Colors we Admire; What we Breathe and Breathe for; What, How, and Why we Digest; the Body we Cherish; the Circulation of Matter.

In the number and variety of striking illustrations, in the simplicity of its style, and in the closeness and cogency of its arguments, Professor Johnston's "Chemistry of Common Life" has as yet found no equal among the many books of a similar character which its success originated, and it steadily maintains its preëminence in the popular scientific literature of the day. In preparing this edition for the press, the editor had the opportunity of consulting Professor Johnston's private and corrected copy of "The Chemistry of Common Life," who had, before his death, gleaned very many fresh details, so that he was able not only to incorporate with his revision some really valuable matter, but to learn the kind of addition which the author contemplated.

D. APPLETON & CO., Publishers,
1, 3, & 5 Bond Street, New York.

Deschanel's Natural Philosophy.

NATURAL PHILOSOPHY:

An Elementary Treatise.

By Professor DESCHANEL, of Paris.

Translated, with Extensive Additions,
By J. D. EVERETT, D. C. L., F. R. S.,
PROFESSOR OF NATURAL PHILOSOPHY IN THE QUEEN'S COLLEGE, BELFAST.

1 volume, medium 8vo. Illustrated by 760 Wood Engravings and Three Colored Plates. Cloth, $5.70.

Published, also, separately, in Four Parts. Limp cloth, each $1.50.

Part I. MECHANICS, HYDROSTATICS, and PNEUMATICS.
" II. HEAT.
" III. ELECTRICITY and MAGNETISM.
" IV. SOUND and LIGHT.

SATURDAY REVIEW.

"Systematically arranged, clearly written, and admirably illustrated, showing no less than 760 engravings on wood and three colored plates. It forms a model work for a class of experimental physics. Far from losing in its English dress any of the qualities of matter or style which distinguished it in its original form, it may be said to have gained in the able hands of Professor Everett, both by way of arrangement and of incorporation of fresh matter, without parting in the translation with any of the freshness or force of the author's text."

ATHENÆUM.

"A good working class-book for students in experimental physics."

WESTMINSTER REVIEW.

"An excellent hand-book of physics especially 'suitable for self-instruction. . . . The work is published in a magnificent style; the woodcuts especially are admirable."

QUARTERLY JOURNAL OF SCIENCE.

"We have no work in our own scientific literature to be compared with it, and we are glad that the translation has fallen into such good hands as those of Professor Everett. . . . It will form an admirable text-book."

NATURE.

"The engravings with which the work is illustrated are especially good, a point in which most of our English scientific works are lamentably deficient. The clearness of Deschanel's explanations is admirably preserved in the translation, while the value of the treatise is considerably enhanced by some important additions. . . . We believe the book will be found to supply a real need."

D. APPLETON & CO., New York.

PRIMERS

IN SCIENCE, HISTORY, AND LITERATURE.

18mo. . . . . Flexible cloth, 45 cents each.

I.—Edited by Professors HUXLEY, ROSCOE, and BALFOUR STEWART.

SCIENCE PRIMERS.

Introductory	T. H. Huxley.
Chemistry	H. E. Roscoe.
Physics	Balfour Stewart.
Physical Geography	A. Geikie.
Geology	A. Geikie.
Physiology	M. Foster.
Astronomy	J. N. Lockyer.
Botany	J. D. Hooker.
Logic	W. S. Jevons.
Inventional Geometry	W. G. Spencer.
Pianoforte	Franklin Taylor.
Political Economy	W. S. Jevons.

II.—Edited by J. R. GREEN, M. A., Examiner in the School of Modern History at Oxford.

HISTORY PRIMERS.

Greece	C. A. Fyffe.
Rome	M. Creighton.
Europe	E. A. Freeman.
Old Greek Life	J. P. Mahaffy.
Roman Antiquities	A. S. Wilkins.
Geography	George Grove.

III.—Edited by J. R. GREEN, M. A.

LITERATURE PRIMERS.

English Grammar	R. Morris.
English Literature	Stopford Brooke.
Philology	J. Peile.
Classical Geography	M. F. Tozer.
Shakespeare	E. Dowden.
Studies in Bryant	J. Alden.
Greek Literature	R. C. Jebb.
English Grammar Exercises	R. Morris.
Homer	W. E. Gladstone.
English Composition	J. Nichol.

(*Others in preparation.*)

The object of these primers is to convey information in such a manner as to make it both intelligible and interesting to very young pupils, and so to discipline their minds as to incline them to more systematic after-studies. In the Science Series some simple experiments have been devised, leading up to the chief truths of each science. By this means the pupil's interest is excited, and the memory is impressed so as to retain without difficulty the facts brought under observation. The woodcuts which illustrate these primers serve the same purpose, embellishing and explaining the text at the same time.

D. APPLETON & CO., Publishers,
1, 3, & 5 Bond Street, New York.