A MANUAL OF THE CHEMISTRY

OF

THE CARBON COMPOUNDS;

OR,

ORGANIC CHEMISTRY.

BY

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PREFACE.

The arrangement adopted in this volume is that which I have followed in my lectures during the last few years. My endeavour has been to render this work as complete a record as possible of the present state of organic chemistry, which, owing to the rapid and brilliant development of this branch of science, is a somewhat difficult task.

Of the immense number of organic compounds now known, only those have been described which have either a special theoretical interest or are of importance in medicine or the arts.

My best thanks are due to my friend, R. S. Dale, B.A., for the aid he has rendered me in writing this book.

C. SCHORLEMMER.

December 1873.

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THE CHEMISTRY OF THE CARBON COMPOUNDS.

INTRODUCTION.

CARBON is one of the most widely distributed elements occurring on our planet. In the free state it is found in two allotropic modifications, as *Graphite* and as *Diamond*. In combination with oxygen, it occurs as *Carbon Dioxide*, forming a small but normal and important constituent of our atmosphere, whilst *Carbonates* are met with in all geological formations, often in immense layers, sometimes forming whole mountain chains.

Far more numerous and varying, however, are the carbon compounds existing in the bodies of plants and animals, *carbon being the most characteristic and important constituent of all organisms.* When any organized structure is heated out of contact with air, carbon is left behind in the form of porous, amorphous charcoal. Animal and vegetable substances are the chief sources from which other carbon compounds are prepared, and the number of these is so great as to far exceed the compounds of the other elements taken together: moreover, new ones are being daily brought to light.

By far the largest proportion of the carbon compounds, and chiefly those occurring ready formed, contain only a few elements; most of them being formed by the union of carbon with hydrogen and oxygen; many also contain nitrogen; some only carbon, hydrogen, and nitrogen, whilst others consist only of carbon and hydrogen.

The substances of which the bodies of plants and animals are built up, as well as most of the compounds that can be obtained from these by chemical changes, exhibit certain peculiarities, enabling us to distinguish them easily from mineral bodies. Formerly chemists believed that the cause of this difference was, that life was necessary to their formation, and that there existed an essential difference between organic and inorganic bodies. Hence chemistry has been divided into organic and inorganic chemistry. At that time it was understood both how to decompose mineral compounds into their elements, and also how to build them up again. With organic bodies, however, it was not so; whilst their composition could easily be ascertained, their synthesis was found to be surrounded by difficulties so great as to appear insurmountable, and hence it was assumed that the elements present in living bodies obeyed laws entirely different from those which rule inanimate nature. It was said that organic bodies might be changed into other organic compounds, but that it was impossible to prepare any such body by synthesis.

The further development of chemistry has shown, however, that such views were erroneous, and as soon as a clearer insight into the chemical constitution of organic compounds was gained, methods were found by which compounds, which hitherto had only been formed by the process of life, could be built up from their constituent elements.

There exist, however, certain organic substances possessing a structure essentially different from that of any inorganic body. This organized structure, which is the sole and direct product of life, is seen in the simple cell, the germ of all living organisms. This cannot be artificially prepared, whereas liquid and crystalline organic compounds have been produced by synthetical methods in such numbers that there can hardly be any doubt that all of them can be built up from their elements.

We have now come to the conviction that the same chemical laws rule animate and inanimate nature, and that the distinctive behaviour which the compounds formed by the vital process exhibit, depends only on the fact that they are carbon compounds. The cause of their peculiar properties is consequently to be looked for in the chemical nature of carbon itself, and we must therefore first enter upon the study of the chemical properties of this element, and compare them with those of the other elements.

QUANTIVALENCE OF THE ELEMENTS.

CHEMICAL NATURE OF CARBON.

Elements combine either in the proportion of their combining weights or in simple multiples of them. To explain this fact, we assume with Dalton that matter is made up of small particles, which are *chemically* indivisible and are therefore called *chemical atoms*. Of these atoms there exist as many kinds as there are elements. Simple bodies consist of the same kind of atoms, all of which have the same weight, whilst the atoms of different elements possess different weights. The ratio existing between these different weights is expressed by the combining weights of the elements, which are hence also called *atomic weights*. By two or more heterogeneous atoms being joined together, a chemical compound is formed. The smallest particle of such a compound consists of a coalition of atoms, only capable of destruction by chemical, not by mechanical means, and this is called a *molecule*. The smallest portion of a simple body also consists of a group of atoms or a molecule, not mechanically divisible.

As our unit for the atomic weights, we use that of hydrogen; its molecule consisting of two atoms. The same element also serves as the unit for the density of gases and vapours. It has now been found that the densities of all gases and vapours are equal to half their molecular weights, and that, consequently, equal volumes of different gases always contain the same number of molecules, or that any molecule in the gaseous state occupies the same space as two parts by weight of hydrogen.

When a chemical change occurs, certain atoms contained in different molecules replace each other. Formerly it was believed that one atom always changed place with another, but we now know that this is not the case, but that one atom of a certain element often replaces two, three, or four atoms of other elements. Hence the atoms of different elements differ in their *quantivalence*.

Hydrogen is distinguished amongst all the elements by its forming the most simple compounds, and for this reason this element is best adapted for ascertaining the quantivalence of other elements, of which those forming volatile hydrides can be divided into four groups:—

Hydrogen.	Hydrogen Chloride.	Hydrogen Bromide.	Hydrogen Iodide.	Hydrogen Fluoride.
$\left.\begin{matrix}H\\H\end{matrix}\right\}$	$\left.\begin{matrix}H\\Cl\end{matrix}\right\}$	$\left.\begin{matrix}H\\Br\end{matrix}\right\}$	$\left.\begin{matrix}H\\I\end{matrix}\right\}$	$\left.\begin{matrix}H\\F\end{matrix}\right\}$

Water.	Hydrogen Sulphide.	Hydrogen Selenide.	Hydrogen Telluride.
$\left.\begin{matrix}H\\H\end{matrix}\right\}O$	$\left.\begin{matrix}H\\H\end{matrix}\right\}S$	$\left.\begin{matrix}H\\H\end{matrix}\right\}Se$	$\left.\begin{matrix}H\\H\end{matrix}\right\}Te$

Ammonia.

$$\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N$$

Hydrogen Phosphide.

$$\left.\begin{matrix}H\\H\\H\end{matrix}\right\}P$$

Hydrogen Arsenide.

$$\left.\begin{matrix}H\\H\\H\end{matrix}\right\}As$$

Hydrogen Antimonide.

$$\left.\begin{matrix}H\\H\\H\end{matrix}\right\}Sb$$

Marsh gas.

$$\left.\begin{matrix}H\\H\\H\\H\end{matrix}\right\}C$$

Silicon Hydride.

$$\left.\begin{matrix}H\\H\\H\\H\end{matrix}\right\}Si$$

Each molecule of the compounds of the first group contains one atom of hydrogen combined with one atom of another element; the elements of the second group unite with two atoms of hydrogen; in the third group, each element requires three, in the fourth group four, atoms of hydrogen to form a molecule.

The same relations hold good when these different elements combine with chlorine, or another member of the first group, instead of with hydrogen.

Chlorine Monoxide.

$$\left.\begin{matrix}Cl\\Cl\end{matrix}\right\}O$$

Hypochlorous Acid.

$$\left.\begin{matrix}Cl\\H\end{matrix}\right\}O$$

Hypobromous Acid.

$$\left.\begin{matrix}Br\\H\end{matrix}\right\}O$$

Phosphorus Trichloride.

$$\left.\begin{matrix}Cl\\Cl\\Cl\end{matrix}\right\}P$$

Arsenic Tribromide.

$$\left.\begin{matrix}Br\\Br\\Br\end{matrix}\right\}As$$

Antimony Trichloride.

$$\left.\begin{matrix}Cl\\Cl\\Cl\end{matrix}\right\}Sb$$

Carbon Tetrachloride.

$$\left.\begin{matrix}Cl\\Cl\\Cl\\Cl\end{matrix}\right\}C$$

Methyl Iodide.

$$\left.\begin{matrix}H\\H\\H\\I\end{matrix}\right\}C$$

Silicon Tetrachloride.

$$\left.\begin{matrix}Cl\\Cl\\Cl\\Cl\end{matrix}\right\}Si$$

Those elements which do not combine with hydrogen may also be divided into such groups by comparing the compounds which they form with chlorine or other elements of the first group.

Potassium Chloride.

$$\left.\begin{matrix}K\\Cl\end{matrix}\right\}$$

Sodium Iodide.

$$\left.\begin{matrix}Na\\I\end{matrix}\right\}$$

Silver Bromide.

$$\left.\begin{matrix}Ag\\Br\end{matrix}\right\}$$

Calcium Chloride.

$$\left.\begin{matrix}Cl\\Cl\end{matrix}\right\}Ca$$

Zinc Bromide.

$$\left.\begin{matrix}Br\\Br\end{matrix}\right\}Zn$$

Magnesium Iodide.

$$\left.\begin{matrix}I\\I\end{matrix}\right\}Mg$$

Boron Chloride.

$$\left.\begin{matrix}Cl\\Cl\\Cl\end{matrix}\right\}Bo$$

Bismuth Chloride.

$$\left.\begin{matrix}Cl\\Cl\\Cl\end{matrix}\right\}Bi$$

Gold Chloride.

$$\left.\begin{matrix}Cl\\Cl\\Cl\end{matrix}\right\}Au$$

Titanium Chloride.	Tin Chloride.	Platinum Chloride.
$\left.\begin{matrix}Cl\\Cl\\Cl\\Cl\end{matrix}\right\}Ti$	$\left.\begin{matrix}Cl\\Cl\\Cl\\Cl\end{matrix}\right\}Sn$	$\left.\begin{matrix}Cl\\Cl\\Cl\\Cl\end{matrix}\right\}Pt$

Thus all the elements may be divided into different groups, according to their power of combining with or replacing hydrogen. Those which combine with this element atom for atom are termed *univalent* elements or *monads*. Those of the second group are *bivalent* or *Dyads*, each atom of them requiring two monad elements to form a molecule. The elements of the nitrogen group, as well as boron and gold, are *trivalent or Triads*; and carbon, silicon, titanium, tin, and platinum, are *quadrivalent* elements or *Tetrads*.

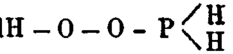
Monad elements form with one another only few and simple compounds, whilst the compounds of the other groups are much more numerous and complicated. Thus chlorine and hydrogen combine only in one proportion, whilst oxygen and hydrogen form two compounds; of oxygen and chlorine we know three compounds; and of oxygen, chlorine, and hydrogen, as many as five compounds.

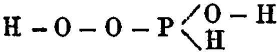
In hydrochloric acid the combining capacity of hydrogen is saturated by chlorine, but if one atom of hydrogen enters into combination with one atom of oxygen, only half the combining capacity of the latter element is *saturated*, and the other half can not only be saturated by hydrogen or by chlorine, but also again by another atom of oxygen; but in the latter case again one of the combining units of oxygen is left free, and in order to form a closed molecule must be combined with a monad element. The constitution of the oxides of hydrogen and the oxides and acids of chlorine is illustrated by the following graphical formulæ:—

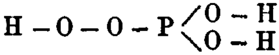
Water	$H - O - H$
Hydrogen Dioxide .	$H - O - O - H$
Chlorine Monoxide .	$Cl - O - Cl$
Chlorine Trioxide . .	$Cl - O - O - O - Cl$
Chlorine Tetroxide .	$Cl - O - O - O - O - Cl$
Hydrochloric Acid .	$Cl - H$
Hypochlorous Acid .	$Cl - O - H$
Chlorous Acid . . .	$Cl - O - O - H$
Chloric Acid . . .	$Cl - O - O - O - H$
Perchloric Acid . .	$Cl - O - O - O - O - H$

In a similar manner we can explain the existence of the different sulphides of potassium and the acids of phosphorus:—

$$K - S - K$$
$$K - S - S - K$$
$$K - S - S - S - K$$
$$K - S - S - S - S - K$$
$$K - S - S - S - S - S - K$$

Hypophosphorous Acid 
$$\mathrm{H - O - O - P}\Big\langle\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}$$

Phosphorous Acid . 
$$\mathrm{H - O - O - P}\Big\langle\begin{matrix}\mathrm{O - H}\\\mathrm{H}\end{matrix}$$

Phosphoric Acid . . 
$$\mathrm{H - O - O - P}\Big\langle\begin{matrix}\mathrm{O - H}\\\mathrm{O - H}\end{matrix}$$

It is thus seen that the atoms of a polyvalent element have the property of combining with each other in different proportions. This property is also possessed by carbon, but in a much greater extent; for whilst in the case of other elements the number of atoms uniting in this way is very limited, *we find it most characteristic of tetrad carbon, that a very large number of atoms can combine with each other to form groups acting in a great number of reactions like a single atom.*

But carbon possesses another peculiarity in common with no other element; *all the units of combining capacity in such a group, which are not saturated by carbon itself, can be saturated with hydrogen.*

Thus, whilst most of the metals do not combine with hydrogen at all, and the non-metallic elements only form one, two, or at the most three compounds with hydrogen, we find that there exists a great number of hydrocarbons, which is daily increased by new discoveries.

The hydrocarbons are not only the most simple of the carbon compounds, but from a theoretical point of view are also the most important, because all the other carbon compounds can be regarded as derivatives of them, and as being formed, by hydrogen being replaced by other elements. Thus a considerable number of compounds found in nature can be prepared artificially from hydrocarbons, and on the other hand, as soon as the constitution of a certain compound is understood, we are in a position to convert it into the hydrocarbon from which it has been theoretically derived. In most of these compounds a part of the hydrogen is replaced by oxygen or by the monad group Hydroxyl HO, and in others by nitrogen, or the monad group NH_2.

However, all the other elements can be artificially introduced into carbon compounds, but there are only a few cases in which all the hydrogen can be substituted. Thus, the number of carbon chlorides is very much smaller than that of the hydrocarbons; with oxygen, carbon forms only two compounds, the monoxide CO and the dioxide CO_2; and with nitrogen it only combines in one proportion to form cyanogen, C_2N_2. From this it follows that the great majority of carbon compounds always contains hydrogen; that there is present in them a residue of the original hydrocarbon.

We may therefore define that part of our science which is generally known as Organic Chemistry as: *The Chemistry of the Hydrocarbons and their Derivatives.*

CONSTITUTION OF THE CARBON COMPOUNDS.

Carbon is a tetrad element: its most simple compound is marsh gas, or methane, CH_4. Of the four hydrogen atoms of this compound, one after the other can be replaced by other elements. For instance, if they are substituted by chlorine, the following bodies are formed:—

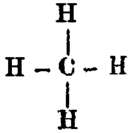
Methane.	Methyl Chloride.	Methene Chloride.	Chloroform.	Carbon Tetrachloride.
CH_4	CH_3Cl	CH_2Cl_2	$CHCl_3$	CCl_4

By replacing the hydrogen by dyad or triad elements, we obtain compounds such as—

Carbon Dioxide.	Carbon Disulphide.	Hydrocyanic Acid.
CO_2	CS_2	CNH

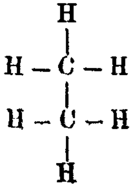
When two atoms of carbon unite with each other, we have as the most simple case two of the eight units of combining capacity saturating each other, six being left free, and thus a hexad group is formed, from which the hydrocarbon C_2H_6 is derived; by linking in the same manner another atom of carbon to the hexad group, we obtain an octad group, &c. The constitution of such groups is illustrated by the following formulæ of the corresponding hydrocarbons:—

CH_4



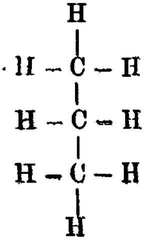
$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ H & - & C & - & H \\ & & | & & \\ & & H & & \end{array}$$

C_2H_6



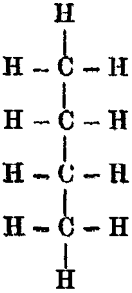
$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ H & - & C & - & H \\ & & | & & \\ H & - & C & - & H \\ & & | & & \\ & & H & & \end{array}$$

C_3H_8



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

C_4H_{10}



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

We are acquainted with a very large number of hydrocarbons constituted in this manner, forming a series in which each higher member contains one atom of carbon and two atoms of hydrogen more than the preceding one, and having the general formulæ C_nH_{2n+2}.

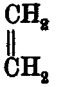
CH_4	Methane.	C_4H_{10} . .	Butane.
C_2H_6 . . .	Ethane.	C_5H_{12} . .	Pentane.
C_3H_8 . . .	Propane.	C_6H_{14} . .	Hexane.

Parallel with this series there run other series containing less hydrogen.

Series C_nH_{2n}.		Series C_nH_{2n-2}.	
C_2H_4	Ethene.	C_2H_2	Ethine.
C_3H_6	Propene.	C_3H_4	Propine.
C_4H_8	Butene.	C_4H_6	Butine.
C_5H_{10}	Pentene.	C_5H_8	Pentine.
C_6H_{12}	Hexene.	C_6H_{10}	Hexine.

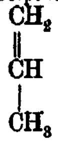
To explain the constitution of these series we must assume that two or more carbon atoms are linked together with more than one unit of combining capacity.

Ethene.



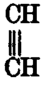
$CH_2{=}CH_2$

Propene.



$CH_2{=}CH{-}CH_3$

Ethine.



$CH{\equiv}CH$

In each of these hydrocarbons we can replace one or more atoms of hydrogen by other elements or radicals, and therefore each forms the starting-point for a number of compounds containing the same number of atoms of carbon in the molecule. If we replace one atom of hydrogen, the compounds thus formed contain in common a group of atoms, having one atom of hydrogen less than the original hydrocarbon, and acting therefore as a monad radical, as the hydride of which the hydrocarbon itself may be regarded.

By acting with chlorine on the hydrocarbons of the first series, hydrochloric acid is formed, and the hydrogen thus removed is replaced by chlorine. By the replacement of one atom of hydrogen, the following series of chlorides of monad radicals is obtained:—

CH_3Cl	Methyl Chloride.	C_4H_9Cl	Butyl Chloride.
C_2H_5Cl	Ethyl Chloride.	$C_5H_{11}Cl$	Pentyl Chloride.
C_3H_7Cl	Propyl Chloride.	$C_6H_{13}Cl$	Hexyl Chloride.

In the same way, by substituting bromine or iodine for hydrogen, we obtain series of bromides and iodides.

Dyad oxygen or triad nitrogen cannot replace one atom of hydrogen, but the monad groups OH and NH_2 can do this. In the former case we obtain a series of important compounds which are the hydroxides of monad radicals and are called alcohols, and in the latter case compound ammonias or amines are formed. Like the hydrocarbons, the chlorides, &c., these new series consist of a number of compounds, each differing from the preceding by the addition of CH_2. Such series are called *homologous*. Compounds are called homologous when they have an analogous constitution and differ in their composition by CH_2 or a multiple thereof.

Homologous Series of Alcohols.		Homologous Series of Amines.	
$CH_3 . OH$	Methyl Alcohol.	$CH_3 . NH_2$	Methylamine.
$C_2H_5 . OH$	Ethyl Alcohol.	$C_2H_5 . NH_2$	Ethylamine.
$C_3H_7 . OH$	Propyl Alcohol.	$C_3H_7 . NH_2$	Propylamine.

Homologous Series of Alcohols.		Homologous Series of Amines.	
$C_4H_9 . OH$	Butyl Alcohol.	$C_4H_9 . NH_2$	Butylamine.
$C_5H_{11} . OH$	Pentyl Alcohol.	$C_5H_{11} . NH_2$	Pentylamine.
$C_6H_{13} . OH$	Hexyl Alcohol.	$C_6H_{13} . NH_2$	Hexylamine.

The oxygen of the alcohols may be replaced by sulphur or other dyad elements, and the nitrogen of the amines by other triads, as phosphorus, arsenic, &c.

In the alcohols, two atoms of hydrogen are easily replaced by one atom of oxygen, and thus the following homologous series of monobasic acids is formed:—

$COH . OH$	Formic Acid.	$C_4OH_7 . OH$	Butyric Acid.
$C_2OH_3 . OH$	Acetic Acid.	$C_5OH_9 . OH$	Valerianic Acid.
$C_3OH_5 . OH$	Propionic Acid.	$C_6OH_{11} . OH$	Caproic Acid.

These acids contain the group hydroxyl OH combined with an oxygenated radical, which, like the alcohol radicals, form a large number of compounds such as—

Acetaldehyde.	Acetyl Chloride.
$C_2OH_3 . H$	$C_2OH_3 . Cl$
Acetamide.	**Thiacetic Acid.**
$C_2OH_3 . NH_2$	$C_2OH_3 . SH$

From the hydrocarbons which contain less hydrogen than those of the first group, similar compounds are derived:—

Propene.	Allyl Alcohol.	Allyl Chloride.	Allylamine.
C_3H_6	$C_3H_5 . OH$	$C_3H_5 . Cl$	$C_3H_5 . NH_2$

Acrylaldehyde.	Acrylic Acid.
$C_3OH_3 . H$	$C_3OH_3 . OH$

Those compounds, in which two atoms of carbon are linked together by more than one of their combining units, possess the characteristic property of being easily transformed into compounds in which the carbon atoms are joined together in as simple a manner as in the methane series. Thus ethine combines with hydrogen to form first ethene, which hydrocarbon, by taking up another molecule of hydrogen, is converted into ethane:—

$$C_2H_2 + H_2 = C_2H_4$$
$$C_2H_4 + H_2 = C_2H_6$$

By the same reaction, allyl compounds yield compounds of the propyl series:—

$$C_3H_5 . OH + H_2 = C_3H_7 . OH$$
$$C_3OH_3 . OH + H_2 = C_3OH_5 . OH$$

Such compounds combine more easily still with the elements of the chlorine group:—

Ethene.		Ethene Dichloride.	Propene.		Propene Bromide.
$C_2H_4 + Cl_2$	=	$C_2H_4Cl_2$	$C_3H_6 + Br_2$	=	$C_3H_6Br_2$

The hydrocarbons of the ethene series behave therefore like *dyad radicals*; their chlorides, &c., can also be obtained by substituting two atoms of chlorine for hydrogen in the members of the methane series:—

Propane. Propene Dichloride.

$$C_3H_8 + 2Cl_2 = C_3H_6Cl_2 + 2HCl$$

The chlorine or bromine in these compounds can, as is the case with the chlorides of the monad radicals, be displaced by other elements or radicals, and thus we obtain alcohols, amines, &c., of dyad radicals:—

Ethene Alcohol.	Ethene-diamine.
$C_2H_4\left\{\begin{array}{l}OH\\OH\end{array}\right.$	$C_2H_4\left\{\begin{array}{l}NH_2\\NH_2\end{array}\right.$

If two atoms of chlorine are replaced by one atom of oxygen, the oxides of these dyad radicals are obtained, and by the substitution of oxygen for hydrogen in the alcohols, acids are formed containing oxygenated dyad radicals:—

Ethene Oxide.	Ethene Alcohol.	Glycollic Acid.	Oxalic Acid.
C_2H_4O	$C_2H_4\left\{\begin{array}{l}OH\\OH\end{array}\right.$	$C_2H_2O\left\{\begin{array}{l}OH\\OH\end{array}\right.$	$C_2O_2\left\{\begin{array}{l}OH\\OH\end{array}\right.$

The hydrocarbons of the ethine series can either combine with two or with four atoms of chlorine, and play the part of dyad as well as of tetrad radicals.

In other compounds we have to assume the existence of triad, pentad, hexad, &c., radicals. Thus glycerin $C_3H_5(OH)_3$ is the alcohol of the radical propenyl C_3H_5, which contains three atoms of hydrogen less than propane, and is therefore a triad radical in which the carbon atoms are linked together exactly as they are in propane; whilst in the monad radical allyl, which has the same composition as propenyl, the carbon atoms are combined in the same manner as in propene C_3H_6. Propenyl and allyl compounds are nearly related to the propyl and propene compounds, and from a member of one group, compounds belonging to another group may be easily obtained. Thus, by the action of chlorine upon propane the chlorides of propyl, propene, and propenyl are formed:—

$$\begin{array}{l}C_3H_8 + Cl_2 = C_3H_7Cl + HCl\\C_3H_8 + 2Cl_2 = C_3H_6Cl_2 + 2HCl\\C_3H_8 + 3Cl_2 = C_3H_5Cl_3 + 3HCl\end{array}$$

When propyl alcohol is heated with sulphuric acid, propene and water are produced:—

$$C_3H_7.OH = C_3H_6 + H_2O$$

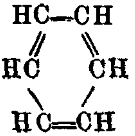
By the action of iodine and phosphorus on glycerin, allyl iodide is formed:—

$$C_3H_5\left\{\begin{array}{l}OH\\OH\\OH\end{array}\right. + P + I = C_3H_5I + PO_3H_3$$

All compounds in which the carbon atoms are linked together in the same manner as in the hydrocarbons of the methane series, form one large group, which has been called the group of the *fatty substances*, because most of the monobasic acids, belonging to it, occur in vegetable and animal fats; and these acids form a homologous series which is very complete and has been long known. The most characteristic property of the members of this group is that they undergo chemical changes principally by *substitution*, i.e. atoms or groups of atoms are taken out and displaced by others.

A second group includes those compounds in which two or more atoms of carbon are linked together with more than one of their combining units. These bodies possess the characteristic property of combining directly with hydrogen, chlorine, &c., and thus by *addition* are changed into compounds belonging to the first group. This group is usually called the group of the *non-saturated* compounds, a term which, however, would imply that these bodies contained carbon atoms with free combining units, an assumption which for several reasons appears improbable.

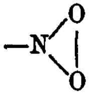
Besides these two groups there exist other groups of carbon compounds, which are richer in carbon than the fatty substances, but these comport themselves in most of their chemical metamorphoses like the latter, and only in a few cases form new compounds by addition, which, however, always contain less hydrogen than fatty bodies. This class of compounds is again subdivided into different groups, the best known of which is that of the *aromatic substances*, this name being derived from the fact that many of them are found in essential oils, balsams, resins, &c. No compound belonging to this group contains less than six atoms of carbon, the most simple hydrocarbon of the group being *benzene* C_6H_6, in which of the twenty-four combining units of carbon, eighteen are taken up by the union of carbon with carbon, whilst the remaining six are combined with hydrogen, thus:—



This linking of the carbon atoms may figuratively be expressed by saying that they are joined together in an annular or closed chain, whilst in the fatty and the non-saturated compounds they form an open chain.

All hydrocarbons contain an even number of atoms of hydrogen; this is, as it will easily be seen, a consequence of carbon being a tetrad. From this fact it follows further *that the sum of the atoms of monad and triad elements contained in the molecule of a carbon compound must also always be an even number.*

The observation that by replacing in a hydrocarbon one or more atoms of hydrogen by other elements, compounds are obtained which contain in common the same residue of the original hydrocarbon, led to the theory of compound radicals. For a time organic chemistry was defined as the *chemistry* of the *compound radicals.* This definition, however, does not hold good, because a great number of inorganic compounds also contain such groups of atoms, which in a great number of reactions remain together, and act as compound radicals. Thus the following compounds contain the radical *nitroxyl* NO_2, which is a monad, nitrogen and oxygen being combined in the following manner:—



Nitrous Acid	NO_2H
Nitric Acid	$NO_2.OH$
Nitroxyl Chloride	NO_2Cl

The dyad radical *Sulphuryl* SO_2 forms the following compounds:—

Sulphuryl Chloride	$SO_2\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.$
Sulphur Trioxide	$SO_2.O$
Hydrosulphurous Acid	$SO_2\left\{\begin{matrix}H\\H\end{matrix}\right.$
Sulphurous Acid	$SO_2\left\{\begin{matrix}H\\OH\end{matrix}\right.$
Sulphuric Acid	$SO_2\left\{\begin{matrix}OH\\OH\end{matrix}\right.$
Hyposulphurous Acid	$SO_2\left\{\begin{matrix}OH\\SH\end{matrix}\right.$

Many phosphorus compounds contain the triad radical Phosphoryl PO:—

Phosphoryl Chloride	$PO\left\{\begin{matrix}Cl\\Cl\\Cl\end{matrix}\right.$
Hypophosphorous Acid	$PO\left\{\begin{matrix}H\\H\\OH\end{matrix}\right.$
Phosphorous Acid	$PO\left\{\begin{matrix}H\\OH\\OH\end{matrix}\right.$
Phosphoric Acid	$PO\left\{\begin{matrix}OH\\OH\\OH\end{matrix}\right.$

The monad group *Uranyl* UO exists in a number of uranium compounds:—

Uranyl Chloride	$UO\,Cl$
Uranyl Nitrate	$UO\,NO_3$
Uranyl Sulphate	$\left.\begin{matrix}UO\\UO\end{matrix}\right\}SO_4$
Uranyl Sulphide	$\left.\begin{matrix}UO\\UO\end{matrix}\right\}S$

Such compound radicals are nothing but groups of atoms which remain unchanged in a great number of reactions, and so far act like a single atom; it is therefore quite a matter of indifference whether compound radicals can exist in the free state or not. Thus the monad and triad alcohol radicals cannot be isolated, but dyad and tetrad radicals exist in the free state, as for example the hydrocarbons of the ethene and ethine series.

Whilst in a great number of metamorphoses the compound radicals remain unaltered, they undergo by other reactions manifold changes. In some of these the carbon group is left intact: thus ethyl alcohol yields by oxidation acetic acid, the radical ethyl C_2H_5 being converted into acetyl C_2H_3O:—

$$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O + O_2 = \left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O + H_2O$$

When we act with chlorine upon propyl chloride, the monad radical propyl is changed into dyad propene:—

$$C_3H_7Cl + Cl_2 = C_3H_6Cl_2 + HCl$$

The dyad radical ethene combines with hydroiodic acid, the iodide of monad ethyl being formed:—

$$C_2H_4 + HI = C_2H_5I$$

But in many other chemical changes the group of carbon atoms is broken up into two or more fragments: thus by heating acetic acid with an excess of caustic soda, it splits up into carbon dioxide and methane:—

$$C_2H_4O_2 = CO_2 + CH_4$$

By the action of the galvanic current, succinic acid is decomposed into ethene, carbon dioxide, and hydrogen:—

$$C_4H_6O_4 = C_2H_4 + 2CO_2 + H_2$$

Such a breaking up of groups of carbon atoms takes place most easily in those derivatives of hydrocarbons in which hydrogen has been displaced by oxygen.

On the other hand, by joining two carbon atoms together, we are able to build up more complicated compounds from simple ones. By heating methyl iodide with zinc, the iodine combines with the metal and methyl with methyl, and we obtain ethane or ethyl hydride:—

$$2CH_3I + Zn = ZnI_2 + C_2H_6$$

By the same reaction ethyl iodide yields butane or butyl hydride:—

$$2C_2H_5I + Zn = ZnI_2 + C_4H_{10}$$

If we replace the chlorine in methyl chloride by cyanogen we obtain acetonitril C_2H_3N, a body which does not behave like a compound of cyanogen and methyl, because it contains the two carbon atoms linked together exactly in the same manner as they are in ethyl and acetyl compounds, and we can in fact easily obtain from acetonitril other ethyl and acetyl compounds.

By these and other similar reactions we are enabled to prepare from compounds containing only one atom of carbon in the molecule, others containing a great number, and thus to build up whole homologous series.

The existence of such series is particularly characteristic of the carbon compounds. The *chemical character* of the different series of hydrocarbons depends on *the manner in which the carbon atoms are linked together*, whilst the *physical properties* of each member depend on the number of carbon atoms it contains. This number may range from one to thirty or more; and in such a case the lowest members of the series are often gaseous at the ordinary temperature, the highest solid, and the intermediate ones liquid (the boiling point rising with the increase of carbon atoms). They nevertheless all resemble each other in chemical properties.

If we now, in all the members of such a series, replace hydrogen by chlorine or another element or compound radical, we obtain other homologous series, the members of which, as might have been expected, possess also varying physical properties, and a very similar chemical character.

A consequence of this is, that whilst the proportionally limited number of compounds of other elements allows us to elucidate the nature and composition of a substance by a few reactions, there exist only a few carbon compounds which can be recognised by qualitative analysis. In most cases it is necessary to obtain the compound to be examined, in a perfectly pure state, to examine its physical properties, and particularly, when the body is volatile, to determine its vapour density; and beyond that, not only to study its chemical properties, but also to find its exact composition by quantitative analysis.

Newly discovered compounds are not the only ones which require such a complete investigation; in many cases well-known bodies can only be identified by determining their quantitative composition and their vapour density.

It is therefore of the greatest importance to be well acquainted with the methods employed for the ultimate analysis of carbon compounds and those in use for the determination of vapour density.

ULTIMATE ANALYSIS OF CARBON COMPOUNDS.

Determination of Carbon and Hydrogen.—To ascertain the presence of carbon in a substance, it is best to convert it into carbon dioxide; most compounds of this element are combustible, and when a sufficient quantity of oxygen is present the whole of the carbon is oxidized to carbon dioxide and the hydrogen to water. This is always the case if the substance is heated to redness with an excess of copper oxide. On this fact Liebig has founded a method for determining carbon and hydrogen quantitatively. To effect this analysis by combustion, a tube of hard Bohemian glass (Fig. 1 A A) is used which is about 50-60 centimetres long, drawn out to a fine closed point at one end and open at the other. One-fourth of the tube is filled with freshly ignited copper oxide and well mixed with a weighed quantity (about 0·2 to 0·3 grams) of the substance by means of a brass wire, one end of which is twisted like a corkscrew (B); more oxide is now added, and the brass wire is well cleaned from every trace of adhering substance until the tube is filled.

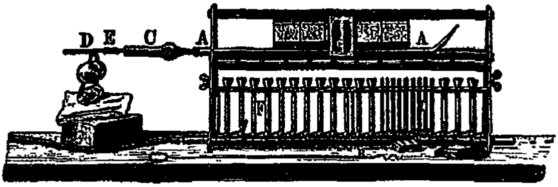


FIG. 1.

The tube (C), which is filled with pieces of porous calcium chloride, by which all the water formed in the combustion is completely absorbed, is now attached to the open end of the tube by means of a tightly fitting cork. The carbon dioxide passes through this tube unabsorbed into a concentrated solution of caustic potash which is contained in the bulb apparatus (D) and connected with the drying tube by a piece of tightly fitting india-rubber tubing (E). Both absorption tubes are carefully weighed before the analysis.

The combustion tube is now placed in a long furnace heated either by charcoal or gas. After the whole arrangement has been found to be perfectly air-tight, the part of the tube near the cork which contains only pure oxide is heated, and when red-hot the portion of the tube containing the substance is gradually heated, the heat being so regulated that a slow evolution of carbon dioxide goes on until the whole of the tube is red-hot. As soon as gas-bubbles cease to enter the potash apparatus, and the potash solution begins to pass back into the bulb nearest to the apparatus (owing to the absorption of carbon dioxide), the source of heat near to the drawn out end is removed, the point of the tube broken off, and air drawn through the whole apparatus by means of an india-rubber tube fixed to the end of the potash bulbs. This operation is necessary in order to pass the aqueous vapour and carbonic dioxide filling the combustion tube into the absorption apparatus. It now only remains to weigh the absorption tubes again, the increase of weight giving respectively the quantities of water and carbon dioxide produced.

If the solution be a *liquid*, it is weighed in a little sealed glass bulb drawn out to a fine point. A little copper oxide is put into the tube first, then the bulb with the point broken off, and afterwards, the tube being filled with the oxide, the combustion is conducted as before.

Substances rich in carbon which are combustible only with difficulty, are, by using this method, often incompletely burnt; the reduced copper gets covered with carbon, which, not being in contact with the oxide, is not burned. In such a case the combustion must be finished by passing a current of pure oxygen through the apparatus, which is easily effected by placing a little fused potassium chlorate at the far end of the combustion tube.

Instead of the method just described another is now generally employed, which is to be recommended on account of its greater simplicity and the more exact results obtained (Fig. 2). A combustion tube is used which is open at both ends, one end being connected with the absorption tubes and the other with a drying apparatus through which either dry air or oxygen can be passed. The part of the tube near the chloride of calcium tube is to two-thirds of its length filled with granulated copper oxide, behind which the substance to be analysed is placed in a platinum boat. In front of and in connection with the absorption tubes is placed an aspirator, in order to ensure the passage of the products of combustion through the absorption tubes, and to prevent them by any chance from passing into the drying apparatus. After the copper oxide has been heated to redness the substance is gradually heated, a slow current of air being passed at the same time through the apparatus in order to drive the products of the combustion into the absorption tubes. As soon as the whole tube is red-hot the current of air is changed for one of oxygen, by which all the carbon left in the platinum boat is completely burned and all the reduced copper re-oxidized.

This method is very convenient, as after each combustion the apparatus is exactly in the same state as it was before; and as soon as it is cooled down a new combustion may be commenced.

If the body to be analysed contains nitrogen, a coil of copper is placed in the fore part of the tube, and kept red-hot in order to decompose any oxides of nitrogen which might be formed. Without this precaution they would be absorbed by the potash, and the weight of the carbon be found too high.

Compounds containing chlorine, bromine, or iodine, yield on combustion these elements in the free state. In order to prevent these getting into the potash bulb, a coil of copper gauze, or, better still, a spiral of silver, is placed in the part of the tube next to the absorption apparatus.

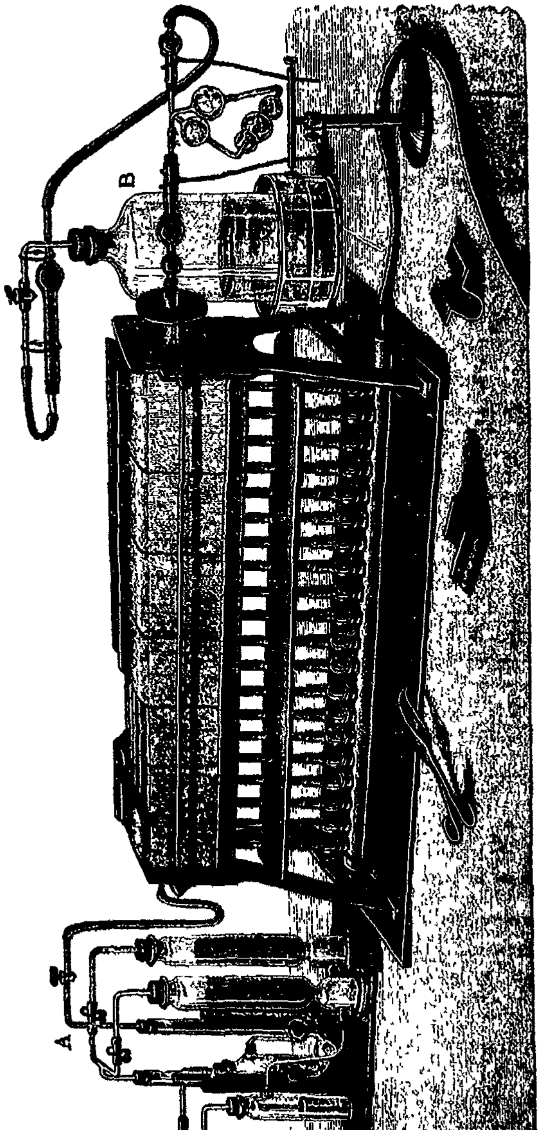


FIG. 2

Instead of using copper oxide, such bodies may be

C c

burned with fused and finely-powdered lead chromate, when lead chloride, &c., is formed. Lead chromate is also employed for the combustion of compounds containing alkali-metals or sulphur, to avoid the formation of alkaline carbonates or sulphur dioxide.

Determination of Nitrogen.—Most carbon compounds containing nitrogen, when heated with caustic soda, yield the whole of this element in the form of *ammonia.* This formation of ammonia is easily rendered evident by heating some cheese or the white of egg with caustic soda. There are, however, some nitrogenous bodies, such as certain cyanogen compounds, which are not acted upon at all by caustic alkalies, whilst others, such as indigo, morphine, quinine, &c., give volatile bases containing carbon. There exist further certain compounds, known as nitro-compounds, which are artificially obtained by the action of nitric acid on different carbon compounds, and which, on heating with caustic alkalis, give either no ammonia or only a part of the nitrogen in this form. To detect nitrogen in such compounds it is necessary to heat them with metallic sodium. A deflagration takes place with the separation of carbon, and sodium cyanide is formed, the presence of which is easily detected by treating the residue with water, and adding to the filtrate first a solution containing a ferric and ferrous salt (a solution of ferrous sulphate which has been exposed to the air answers well for this purpose), and then an excess of hydrochloric acid, to dissolve the oxides of iron, whilst Prussian blue is left behind. Very small quantities of nitrogen can be found by means of this method. In this case the liquid appears green after the addition of the hydrochloric acid, but after standing for some time blue flakes collect together.

For the quantitative determination of nitrogen two methods are in use. Compounds which give off all their nitrogen in the form of ammonia are heated in a combustion tube (Fig. 3) with soda-lime, which is prepared by slacking lime with a solution of caustic soda and heating the powder to redness. This mixture does not fuse at a red heat, and thus prevents the glass from being destroyed. The ammonia formed is absorbed by hydrochloric acid contained in a bulb apparatus, and its weight determined by adding platinic chloride to the solution and weighing the ammonium-platinic chloride $(NH_4Cl)_2 + PtCl_4$ thus formed. This simple and exact method, which was originally proposed by Varrentrapp and Will, can also be employed for such substances as indigo, quinine, &c., since the volatile bases yielded by these compounds are compound ammonias, forming with platinic chlorides also double salts, which, like the ammonium salt, contain two atoms of nitrogen for each atom of platinum. But in this case the double salt is not weighed, but is ignited, and the quantity of platinum left behind determined. It is safer also, when only ammonia has been formed, to find the weight of the platinum by ignition, as the double salt may have volatile carbon compounds adhering to it.

If the nitrogen cannot be completely converted into ammonia, it must be obtained in the free state To effect this the compound is burned with copper oxide, or, better, a mixture of copper oxide and mercuric oxide, in a tube, the fore part of which is filled with red-hot metallic copper. Previous to the combustion all the air must be driven out of the apparatus, which is easily done by placing some magnesite in the closed end of the tube, and heating it until all the gas given off is completely absorbed by caustic potash. The mixture of nitrogen and carbon dioxide given off during the combustion is

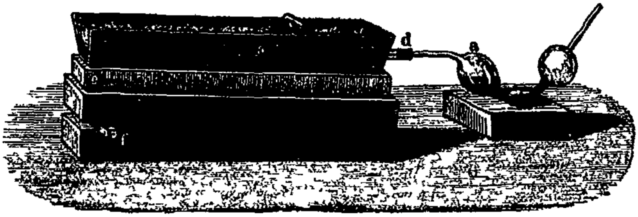


FIG 3

collected over mercury in a wide graduated glass tube, and the nitrogen which remains in the combustion tube when the combustion is finished also driven in the graduated tube by heating the magnesite again. After absorbing the carbon dioxide by caustic potash, the volume of the remaining nitrogen is read off, and from it, measured under given circumstances of temperature and pressure, its weight can be easily calculated.

Determination of other Elements.—Compounds containing *chlorine, bromine, or iodine*, are heated in a narrow combustion tube with pure caustic lime. After cooling, the contents of the tube are dissolved in dilute nitric acid, and the quantity of chlorine, &c., determined by precipitation with silver nitrate. Chlorine may also be converted into silver chloride by heating the substance to be analysed in a sealed glass tube with nitric acid and silver nitrate. To ensure complete oxidation it is advisable to add some potassium dichromate. There exist a few chlorine compounds, which are decomposed by water, with the formation of hydrochloric acid; others yield the whole of the chlorine by bringing them in contact with water and sodium amalgam. From these solutions all the chlorine is precipitated by silver nitrate.

Sulphur and phosphorus are determined by heating the substance with pure nitre and sodium carbonate, or by oxidizing it with nitric acid in sealed tubes, sulphuric or phosphoric acid being formed, which are estimated by known methods.

In a similar way *boron, silicon, arsenic*, &c., are determined. Compounds containing *metals* leave on ignition the metal either in the free state as silver, gold, platinum, or as an oxide or carbonate. Sometimes it is preferable to oxidize the compound with nitric acid or with a mixture of nitre and sodium carbonate. The metallic compounds thus formed are converted according to well-known methods of quantitative analysis into compounds fit for weighing.

Oxygen. cannot be determined directly, but its quantity is always found by difference; by subtracting all the constituents which have been directly estimated from the total weight of the substance taken, the difference gives the weight of the oxygen.

Calculation of the Analysis.—In order to compare the results of different analyses the percentage composition is first calculated as follows:—

(1) 0·1460 grams of hexane yielded, by combustion with copper oxide, 0·4490 of carbon dioxide and 0·2135 water.

Now, as 44 parts by weight of carbon dioxide contain 12 parts of carbon, we find the weight of carbon by multiplying by $\frac{12}{44}$ or $\frac{3}{11}$, and the weight of the hydrogen is obtained by dividing the weight of the water by 9. The following equations therefore give the percentage of carbon and hydrogen in hexane:—

$$\frac{0{\cdot}449 \times 3 \times 100}{0{\cdot}146 \times 11} = 83{\cdot}8.$$

$$\frac{0{\cdot}2135 \times 100}{0{\cdot}146 \times 9} = 16{\cdot}3.$$

100 parts of hexane consist therefore of—

Carbon	83·8
Hydrogen	16·3
	100·1

(2) 0·395 grams of acetic acid gave 0·580 of carbon dioxide and 0·235 of water. 100 parts contain therefore—

Carbon	40·0
Hydrogen	6·6

As these numbers do not add up to 100, the difference must be caused by the presence of oxygen, for qualitative analysis has shown that acetic acid does not contain any other elements but these three. Its percentage composition is therefore—

Carbon	40·0
Hydrogen	6·6
Oxygen	53·4
	100·0

(3) The analysis of caffeine, an organic base contained in coffee and tea, gave the following results:—

0·3827 of substance gave on combustion with copper oxide in presence of metallic copper 0·6948 of carbon dioxide and 0·1800 of water.

0·1350 of substance was heated with soda lime, and the ammonia (or compound ammonia) evolved was absorbed by hydrochloric acid.

To this solution platinic chloride was added, and, after evaporation on a water-bath, the excess of platinic chloride was washed out with alcohol. On igniting the remaining double salt, 0·2750 of platinum was left behind. Now as the salt $(NH_4Cl)_2 + PtCl_4$ contains 2 atoms or 28 parts by weight of nitrogen for each atom of platinum, or 197·5 parts by weight, 100 parts of caffeine contain :—

$$\frac{0{\cdot}2750 \times 28 \times 100}{0{\cdot}1350 \times 197{\cdot}5} = 28{\cdot}9 \text{ parts of nitrogen.}$$

If we calculate the percentage of carbon and hydrogen as above, we find the following percentage composition of caffeine :—

Carbon	49·5	
Hydrogen	5·2	
Nitrogen	28·9	
Oxygen	16·4	by difference.
	100·0	

The methods employed for determining the molecular formula from the analytical data will be hereafter explained, If the substance be volatile, this can be easily done by the determination of its vapour density.

DETERMINATION OF THE VAPOUR DENSITY.

Two methods are employed for determining the vapour density: we ascertain either the weight of a given volume of vapour, or we find the *volume* of a given weight of vapour.

(1) *Dumas' method.*—In the first process a thin glass globe is employed of 150—300 cubic centimetres in capacity, provided with a neck finely drawn out. The exact weight of this globe filled with dry air having been found, and the temperature during the weighing noted, 5—10 grams of the substance are introduced, and the globe then heated in an oil or paraffin bath (Fig 4) to a temperature at least 30° above the boiling point of the substance. The reason for this is that vapours obey the laws of expansion by heat and by pressure only at a temperature considerably above the boiling-point. The air in the globe is expelled by the vapour of the boiling substance, and as soon as vapour ceases to issue from the neck, the orifice is sealed before the blowpipe, the temperature of the oil bath being read off at the same time. After cooling, the previously well-cleaned globe is weighed again and the sealed point broken off under mercury, which rushes into the globe, owing to the condensation of the vapour, and completely fills it, if the experiment has been properly conducted.

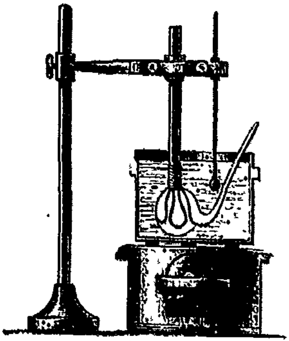


FIG. 4.

To find the volume of the mercury which now fills the globe, it is poured into a graduated cylinder, and thus the capacity of the globe ascertained. From the numbers thus found the density is calculated as follows; as an example we again take hexane:—

Weight of globe with air at 15·5° = 23·449 grams
Ditto ditto vapour at 110° = 23·720 „
Capacity of globe . . . . = 178 cb. cm.

1 cb. cm. of air at 0° weighs 0·001293 grams; 178 cb. cm. at 15·5° weigh therefore—

$$\frac{0·001293 \times 178 \times 273}{288·5} = 0·218.$$

The weight of the vacuous globe is therefore 23·449 − 0·218 = 23·231 and that of the vapour 23·720 − 23·231 = 0·489.

1 cb. cm. of hydrogen at 0° weighs 0·00008936 grams, and 178 cb. cm. at 110° weigh—

$$\frac{0·00008936 \times 273 \times 178}{383} = 0·01134.$$

By dividing the weight of the vapour by this number, we obtain the vapour density of hexane—

$$\frac{0·489}{0·01134} = 43·1.$$

As during the experiment the height of the barometer and the temperature of the air do not change at all, or only very inconsiderably, corrections for pressure and temperature are only necessary when a very exact determination is required, which is however never the case when the vapour density is only used as a means for finding the molecular formula.

Gay-Lussac's method.—A high narrow bell-jar (Fig. 5, C) divided into cb. cm. is filled with dry mercury and inverted into an iron vessel (V) containing mercury. The substance, of which only about a decigram is required, is weighed in a very small and thin glass bulb, or, better, in a little tube provided with a well-ground stopper, and this is allowed to ascend in the jar, the latter being surrounded by a wide glass cylinder, which is open at both ends and filled with water. The iron vessel is now heated by gas or charcoal. By the expansion caused by the heat the bulb either bursts or the stopper is driven out of the tube, and the liquid is soon converted into vapour. To effect an equal distribution of heat, the water is continually moved by means of a stirrer (*p*, *m*, *n*). As soon as the temperature has reached the point at which the determination is to be made, the volume of the vapour, the temperature of the water, and the height of the barometer are noted, and at the same time the temperature of the air and the difference between the height of the mercury inside and outside the globe ascertained.

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A determination of the vapour density of pentane made by this method gave the following results:—

Weight of pentane	0·101
Temperature of air	16°
Temperature of vapour	91°
Volume of vapour	59·5 cb. cm.
Height of barometer	752 mm.
Difference of level	220 mm.

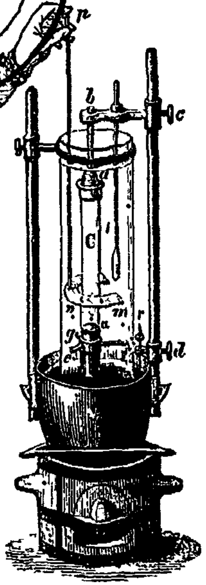


Fig. 6.

The pressure inside the bell-jar was consequently equal to that of a column of mercury of 752 mm. at 16° minus that of a column of 220 mm. at 91°. In order to be able to subtract one from the other we must first reduce them to the same temperature. The coefficient of expansion of mercury is 0·00018; the heights at 0° would therefore be—

$$\frac{752}{1 + (0·00018 \times 16)} = 749·9.$$

$$\frac{220}{1 + (0·00018 \times 91)} = 216·4.$$

The pressure inside the bell-jar was therefore—

$$749·9 - 216·4 = 533·5.$$

59·5 cb. cm. of pentane weigh at 91°, and under a pressure of 533·5 mm. of mercury, 0·101 grams. An equal volume of hydrogen weighs under the same conditions—

$$\frac{0·00008936 \times 59·5 \times 533·5 \times 273}{760 \times 364} = 0·0027992 \text{ grams},$$

and the vapour of density of pentane is—

$$\frac{0·101}{0·0027992} = 36.$$

This method can only be employed conveniently when the substance boils below 100°. If such determinations have to be made above this temperature, oil must be used in the place of water; but the higher the temperature rises, the more difficult it is to cause the whole of the liquid to be uniformly heated, and besides there is great danger of poisonous mercury vapour being given off. But as this method possesses the great advantage of requiring very little substance, whilst by Dumas' method several grams are lost in driving the air out, several endeavours have been made to modify Gay-Lussac's method, so that it might also be employed for high boiling bodies. Of the different modifications, that described by Hofmann has begun to come into general use, as the process is simple and easily effected.

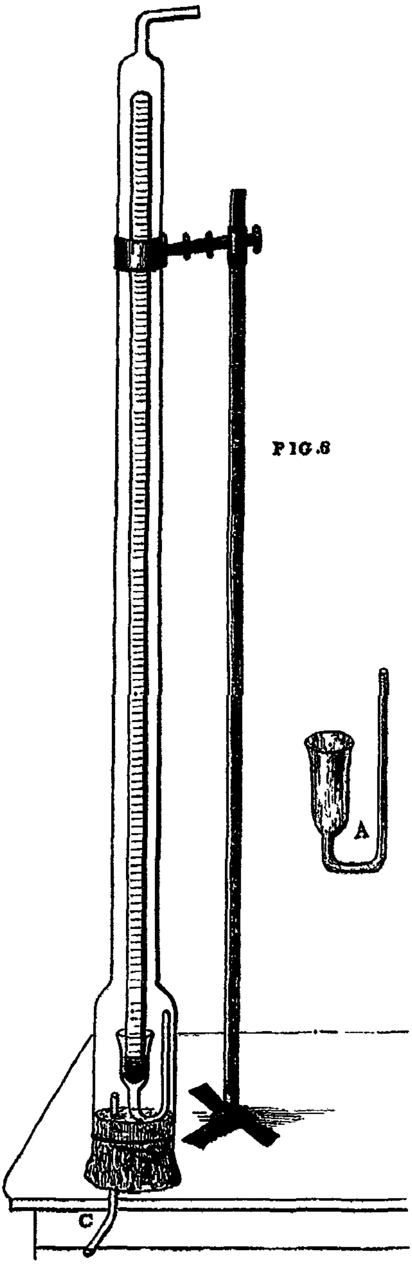


FIG. 6

The apparatus (Fig. 6) consists of a glass tube one metre in length, and about 20 mm. wide, closed at one end and calibrated. This tube is filled with mercury and stands in the little cup (A), also containing mercury. A vacuum is thus obtained, in which the substance (about a decigram) contained in a very small stoppered tube is introduced. The long tube is surrounded by another tube, 30—40 mm. wide, drawn out at the upper end, and widening out at the lower end, which rests on a large cork provided with an open narrower tube (C). Through the upper end of the wider tube the vapour of a liquid having a constant boiling-point is passed. As the vapour of the substance of which the density is to be determined forms *in vacuo*, the boiling-point of the substance is so much lowered that the vapour densities of bodies boiling at 150° and even higher may be determined by means of steam. For producing higher temperatures, amyl alcohol (boiling-point 132°), oil of turpentine (b. p. 160°), or aniline (b. p. 182°), are used, the vapour of these substances escaping, together with the replaced mercury, through the tube (C), which may be connected with a condenser. When the liquid used for heating, boils briskly, the space between the inner and outer tubes soon reaches a constant temperature, and as soon as the volume of the vapour remains constant, the height of the mercurial column, of the barometer, and also the temperature of the air are observed, and from these numbers the vapour density is calculated as before. At higher temperatures the tension of mercury vapour must be taken into consideration.

DETERMINATION OF THE MOLECULAR FORMULA.

The vapour of hexane is, as we have seen, 43·1 times heavier than hydrogen; the molecular weight of this hydrocarbon is consequently $43{\cdot}1 \times 2 = 86{\cdot}2$. Now, as we know its percentage composition, we can easily calculate how much carbon and hydrogen are contained in 86·2 parts by weight:—

$$\frac{83{\cdot}8 \times 86{\cdot}2}{100} = 72{\cdot}23, \text{ or } 6 \times 12 \text{ parts of carbon,}$$

$$\frac{16{\cdot}3 \times 86{\cdot}2}{100} = 14{\cdot}15 \text{ parts of hydrogen.}$$

$$\begin{array}{r}C_6 = 72\\ H_{14} = 14\\ \hline 86\end{array}$$

The molecular weight of hexane is 86, and its formula C_6H_{14}. The discrepancy between the numbers found and those calculated from the formula is caused by unavoidable experimental errors, which, however, being within certain limits, have no disturbing influence.

The vapour density of pentane is 36, and its molecular weight 72. The percentage composition of this hydrocarbon was found to be—

Carbon	83·3
Hydrogen	16·7
	100·0

One molecule therefore contains—

$$\frac{83{\cdot}3 \times 72}{100} = 59{\cdot}976 \text{ or } 5 \times 12 \text{ parts of carbon,}$$

$$\frac{16{\cdot}7 \times 72}{100} = 12{\cdot}0 \text{ parts of hydrogen,}$$

and its molecular formula is C_5H_{12}.

A great number of carbon compounds are acids. To find the molecular weight of such a compound we have only to ascertain the basicity of the acid, and then to determine the quantity of a metal contained in one of its anhydrous normal salts. The silver salts are generally best adapted for this purpose, as they usually crystallize without water, and moreover can be easily obtained in a pure state.

Acetic acid is monobasic; 100 parts of silver acetate leave on ignition 64·67 parts of pure silver; the molecular weight of this salt is therefore—

$$\frac{100 \times 108}{64{\cdot}7} = 167.$$

Silver acetate differs from acetic acid by containing one atom of silver in the place of one atom of hydrogen, and the molecular weight of the acid is therefore—

$$(167 - 108) + 1 = 60.$$

100 parts of acetic acid contain—

Carbon	40·0
Hydrogen	6·6
Oxygen	59·4
	100·0

Consequently, one molecule consists of—

Carbon . . .	24 $= 2 \times 12 = 2$	atoms of	carbon.
Hydrogen . .	3·96 $= 4 \times 1 = 4$	„	hydrogen.
Oxygen . .	32·04 $= 2 \times 16 = 2$	„	oxygen.

The molecular formula of acetic acid is therefore $C_2H_4O_2$, and that of silver acetate $C_2H_3AgO_2$.

Meconic acid, a compound found in opium, is a polybasic acid. On adding silver nitrate to its aqueous solution, a white silver salt is precipitated; but when silver nitrate is added to a solution neutralized by ammonia, a yellow insoluble salt is obtained. The composition of the acid and the two silver salts is as follows:—

	Meconic Acid.	White Silver Salt.	Yellow Silver Salt.
Carbon . . .	42·0	20·2	15·9
Hydrogen . .	2·0	0·5	0·2
Oxygen . . .	56·0	27·0	21·9
Silver	—	52·3	62·0
	100·0	100·0	100·0

If we divide these numbers, respectively, by the atomic weights of the elements, we obtain the relation between the number of atoms of the constituents—

$$42 : 12 = 3{\cdot}5$$
$$2 : 1 = 2$$
$$56 : 16 = 3{\cdot}5$$

The most simple formula of meconic acid deducted from these numbers is $C_7H_4O_7$, but whether this, or a multiple of it, expresses the molecular formula cannot be decided by analysis. In the two salts different quantities of hydrogen are replaced by silver. The white salt contains for each seven atoms of carbon—

$$\frac{0{\cdot}5 \times 84}{20{\cdot}2} = 2{\cdot}1 \text{ parts, or 2 atoms of hydrogen,}$$

$$\frac{52{\cdot}3 \times 84}{20{\cdot}2} = 217 \text{ parts, or 2 atoms of silver.}$$

In the yellow salt we find—

$$\frac{0{\cdot}2 \times 84}{15{\cdot}9} = 1{\cdot}05 \text{ parts of hydrogen,}$$

$$\frac{62{\cdot}0 \times 84}{15{\cdot}9} = 327{\cdot}5 \text{ parts, or 3 atoms of silver.}$$

From this we conclude that the acid is tribasic, and that the formula $C_7H_4O_7$ represents a molecule; and, as a further confirmation, we find that we also know acid salts containing only one atom of a monad metal. The molecular formulæ of the above compounds are therefore—

Meconic acid	$C_7H_4O_7$
White salt	$C_7H_2Ag_2O_7$
Yellow salt	$C_7HAg_3O_7$

A great number of carbon compounds containing nitrogen are bases, which combine with acids like ammonia; some are monacid bases, others are polyacid. To find the molecular weight of such a compound, we have only to ascertain the quantity of acid contained in an anhydrous normal salt, or, better still, to find the quantity of platinum present in the double salts, formed by the combination of the hydrochloride with platinic chloride, and which, like ammonium-platinic chloride, contain two molecules of hydrochloric acid for each molecule of platinic chloride.

Caffeine is a monacid base; its platinum double salt contains two molecules of caffeine, and two molecules of hydrochloric acid, combined with one molecule of platinic chloride; 100 parts of this compound leave on ignition 24·6 per cent. of platinum; consequently, to find out in how much of the platinum salt one atom or 197·5 parts of platinum are contained, we have—

$$\frac{197{\cdot}5 \times 100}{24{\cdot}6} = 806{\cdot}9.$$

From this we find the molecular weight of caffeine by the equation—

$$2x + (2 \times 36{\cdot}5) + 339{\cdot}5 = 806{\cdot}9$$
$$x = 197{\cdot}2.$$

As we know the percentage composition of this base, we can easily find its molecular formula:—

$$\frac{197{\cdot}2 \times 49{\cdot}5}{100} = 97{\cdot}6 \text{ of carbon.}$$

$$\frac{197{\cdot}2 \times 5{\cdot}2}{100} = 10{\cdot}3 \text{ of hydrogen.}$$

$$\frac{197{\cdot}2 \times 28{\cdot}9}{100} = 57{\cdot}0 \text{ of nitrogen.}$$

$$\frac{197{\cdot}2 \times 16{\cdot}4}{100} = 32{\cdot}3 \text{ of oxygen.}$$

One molecule of caffeine consists, therefore, of—

$$\frac{97 \cdot 6}{12} = 8 \cdot 1 \text{ atoms of carbon}$$

$$\frac{10 \cdot 3}{1} = 10 \cdot 3 \text{ atoms of hydrogen.}$$

$$\frac{57}{14} = 4 \cdot 1 \text{ atoms of nitrogen.}$$

$$\frac{32 \cdot 3}{16} = 2 \cdot 0 \text{ atoms of oxygen.}$$

As these numbers must be simple multiples, the formula of caffeine is $C_8H_{10}N_4O_2$.

The largest number of carbon compounds are neither acids nor bases, and when the body under examination is neither volatile nor capable of forming definite compounds, its molecular weight can be ascertained only by an exact study of its chemical metamorphoses. Thus, grape-sugar has the same percentage composition as acetic acid, its most simple formula being CH_2O. It belongs to the so-called non-saturated compounds, and combines with hydrogen to form mannite $C_6H_{14}O_6$, an alcohol of the hexad radical C_6H_8, being hexane C_6H_{14}, in which six atoms of hydrogen are replaced by six of hydroxyl $C_6H_8(OH)_6$. This is proved by the fact that we can easily transform it into hexane by the substitution of hydrogen for hydroxyl. From this we conclude that grape-sugar likewise contains six atoms of carbon in the molecule, and has the molecular formula $C_6H_{12}O_6$.

Starch contains in 100 parts—

Carbon	44·44
Hydrogen	6·18
Oxygen	49·38
	100·00

By dividing these numbers by their atomic weights we obtain the following relation between the number of atoms of the constituent elements:—

$$\frac{44 \cdot 44}{12} = 3 \cdot 70$$

$$\frac{6 \cdot 18}{1} = 6 \cdot 18$$

$$\frac{49 \cdot 38}{16} = 3 \cdot 09$$

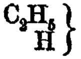
The most simple relation between these numbers is 6 : 10 : 5; but as we have not so far been able to ascertain the molecular weight of starch, we use the for the present the most simple formula, or as the whole chemical character of starch shows that it must have a very high molecular weight, we write the formula $(C_6H_{10}O_5)_x$.

EMPIRICAL, RATIONAL, AND CONSTITUTIONAL FORMULÆ.

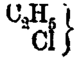
The simplest mode of expressing the composition of a body is to write side by side the symbols and numbers of the constituent atoms :—

C_2H_6	. . Ethane.	$C_2H_3ClO_2$	Chloracetic Acid.
C_2H_5Cl .	. Ethyl Chloride.	$C_4H_8O_2$	. Ethyl Acetate.
C_2H_6O .	. Ethyl Alcohol.	C_2H_4 .	. Ethene.
C_2H_7N .	. Ethylamine.	$C_2H_4Cl_2$	. Ethene Chloride.
$C_4H_{10}O$.	. Diethyl Ether.	$C_2H_6O_2$	. Ethene Alcohol.
$C_2H_4O_2$	. Acetic Acid.	$C_2H_4O_3$	. Glycollic Acid.
C_2H_3OCl	. Acetyl Chloride.	$C_2H_2O_4$	. Oxalic Acid.

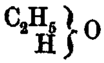
Such formulæ are called *empirical formulæ*. But as the number of carbon compounds is so very large, and as there exists amongst them a considerable number of *Isomerides*, i.e. compounds having the same percentage composition but possessing very different physical and chemical properties, it has been found necessary to use others as well as these empirical formulæ, for the purpose of giving an idea of the chemical character of the body, or to express the relation it bears to other compounds. We call such formulæ *rational formulæ*. Thus, all the ethyl compounds contain the monad radical C_2H_5, and we can represent those contained in the table given above as follows :—



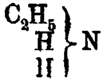
$\left.\begin{matrix} C_2H_5 \\ H \end{matrix}\right\}$ Ethane or Ethyl Hydride.



$\left.\begin{matrix} C_2H_5 \\ Cl \end{matrix}\right\}$ Ethyl Chloride.

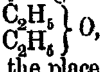


$\left.\begin{matrix} C_2H_5 \\ H \end{matrix}\right\} O$ Ethyl Alcohol.



$\left.\begin{matrix} C_2H_5 \\ H \\ H \end{matrix}\right\} N$ Ethylamine.

These formulæ express that, when we replace, for instance, in ethane one atom of hydrogen by one of chlorine, we obtain ethyl chloride: and that, by substituting the chloride by monad hydroxyl or the monad group NH_2, ethyl alcohol or ethylamine are formed. The formula of alcohol further indicates that its constitution is analogous to water, and that it may be regarded as water in which hydrogen has been replaced by ethyl. From the rational formula of ethylamine it follows that it has a constitution similar to that of ammonia. By replacing the hydrogen in the hydroxyl of alcohol by ethyl we obtain diethyl ether $\left.\begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix}\right\} O$, which may be regarded as water in which ethyl occupies the place of hydrogen.

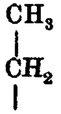


By acting on alcohol with oxidizing agents, two atoms of hydrogen are taken out and their places are occupied by one atom of oxygen, acetic acid being formed, which stands in the same relation to acetyl chloride as alcohol does to ethyl chloride. Acetic acid contains like alcohol the group OH, the hydrogen of which can be replaced by ethyl, ethyl acetate being formed. These acetyl compounds can therefore be represented by the following rational formulæ:—

$$\left.\begin{matrix} C_2H_3O \\ H \end{matrix}\right\} O \text{ Acetic Acid.} \qquad \left.\begin{matrix} C_2H_3O \\ Cl \end{matrix}\right\} \text{ Acetyl Chloride.}$$

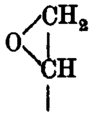
$$\left.\begin{matrix} C_2H_3O \\ C_2H_5 \end{matrix}\right\} O \text{ Ethyl Acetate.}$$

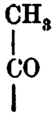
The monad radical acetyl is contained in a large number of compounds; it is derived from ethyl by the substitution of two atoms of hydrogen by one of oxygen. The constitution of ethyl may be represented in the following manner:—



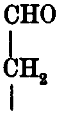
$$\begin{matrix} CH_3 \\ | \\ CH_2 \\ | \end{matrix}$$

What is now the constitution of acetyl? It may be obtained from ethyl in three different ways; either each of the two carbon atoms loses one atom of hydrogen, or the oxygen combines with only one of the two carbon atoms, thus:—





$$\begin{matrix} CH_3 \\ | \\ CO \\ | \end{matrix}$$

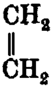


$$\begin{matrix} CHO \\ | \\ CH_2 \\ | \end{matrix}$$

Now all transformations of acetic acid and other acetyl compounds show, that acetyl contains the group CH_3, from which it follows that the second formula represents the constitution of acetyl, and to express this we may write the acetyl compounds in the following way:—

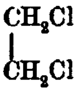
$$\left.\begin{matrix} CH_2 . CO \\ H \end{matrix}\right\} O \text{ Acetic Acid.} \qquad \left.\begin{matrix} CH_3 . CO \\ Cl \end{matrix}\right\} \text{ Acetyl Chloride.}$$

By taking two atoms of hydrogen out of ethane we produce ethene C_2H_4, in which one carbon atom is linked to the other with two combining units:—



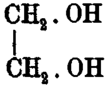
$$\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix}$$

This hydrocarbon combines readily with chlorine, ethene dichloride being formed, in which the carbon atoms are linked together again as they were in ethane:—



$$\begin{matrix} CH_2Cl \\ | \\ CH_2Cl \end{matrix}$$

On replacing the chlorine by hydroxyl we obtain ethene alcohol:—



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

The constitution of the ethene compounds may also be expressed in a more simple way, thus:—

$$C_2H_4\left\{\begin{matrix} Cl \\ Cl \end{matrix}\right. \qquad C_2H_4\left\{\begin{matrix} OH \\ OH \end{matrix}\right.$$

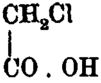
which means that both these compounds contain the dyad radical ethene.

Ethene alcohol yields by oxidation glycollic acid, a compound which can also be obtained from acetic acid. By the action of chlorine on the latter compound, chloracetic acid is formed, one atom of chlorine substituting one atom of hydrogen in the group CH_3. When chloracetic acid $\left.\begin{matrix} CH_2Cl.\,CO \\ H \end{matrix}\right\} O$ is acted upon by caustic potash, the chlorine is replaced by hydroxyl, and potassium chloride and glycollic acid are formed:—

$$\left.\begin{matrix} CH_2Cl\,.\,CO \\ H \end{matrix}\right\} O + KOH = \left.\begin{matrix} CH_2(OH)\,CO \\ H \end{matrix}\right\} O + KCl$$

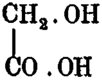
By further oxidation of glycollic acid we obtain oxalic acid, the two remaining atoms of hydrogen of the ethene being substituted by oxygen. The constitution of these different acids we may represent thus:—

Chloracetic Acid.



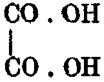
$$\begin{array}{l} CH_2Cl \\ | \\ CO . OH \end{array}$$

Glycollic Acid.



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

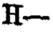
Oxalic Acid.



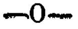
$$\begin{array}{l} CO . OH \\ | \\ CO . OH \end{array}$$

In some cases it is convenient to resolve such *constitutional formulæ* still further, in order to explain cases of isomerism, &c. In order to do this we may represent the quantivalence of elements by straight lines, thus:—

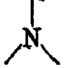
Hydrogen.



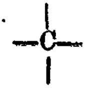
Oxygen.



Nitrogen.

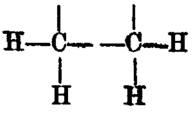


Carbon.

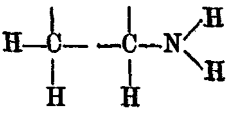


And by aid of these symbols the following graphical formulæ are arrived at:—

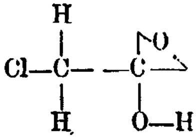
Ethane.



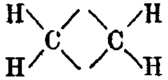
Ethylamine.



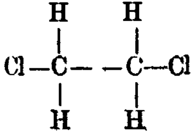
Chloracetic Acid.



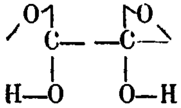
Ethone.



Ethene Dichloride.



Oxalic Acid.



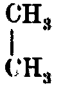
It need hardly be mentioned that such formulæ are not intended to express how the atoms are arranged in space, because of this we are totally ignorant; they simply are intended to give an idea of the manner in which the attractive forces of the atoms, forming the molecule, are distributed.

ISOMERISM.

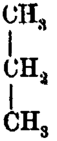
Carbon compounds having the same percentage composition, but differing in their physical and chemical properties, are called *Isomerides;* they are divided into three groups.

(1) *Isomerism proper.*—The isomeric compounds belonging to this division contain the same number of carbon atoms linked together. It is easily understood that isomeric hydrocarbons of the marsh-gas series can only be produced by the carbon atoms being differently grouped, and that of the three first members no isomerides are possible.

CH_4

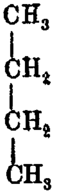


$CH_3{-}CH_3$

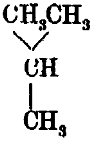


$CH_3{-}CH_2{-}CH_3$

The fourth member C_4H_{10} is derived from the third by methyl taking the place of one atom of hydrogen. Now this substitution can either take place in one of the two methyl groups of propane, or in the group CH_2; consequently two isomerides C_4H_{10} are possible, and both are known:—

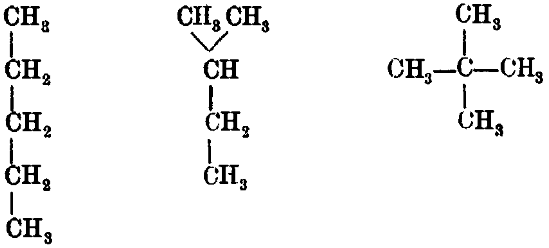


$CH_3{-}CH_2{-}CH_2{-}CH_3$



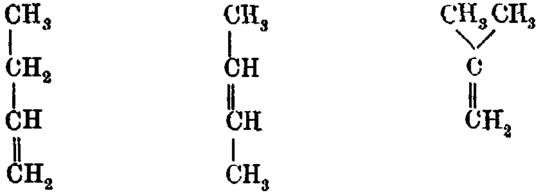
$(CH_3)_2CH{-}CH_3$

Of the fifth member C_5H_{12} three isomeric forms are possible, which are also known :—



Amongst the higher members the number of possible isomerides increases rapidly.

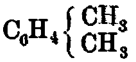
In the same way the isomerides existing amongst the non-saturated hydrocarbons are constituted, but the number of isomerides which may exist in these groups is much larger than those of the marsh-gas series, because hydrogen may be wanting in different places. Thus three isomeric forms of C_4H_8 are possible :—



The isomeric hydrocarbons of other series are produced by similar causes; thus from benzene C_6H_6 a great number of hydrocarbons are derived by hydrogen being replaced by alcohol radicals.

If, for instance, ethyl be substituted for one atom of hydrogen, we obtain ethyl-benzene, which is isomeric with dimethyl-benzene :—

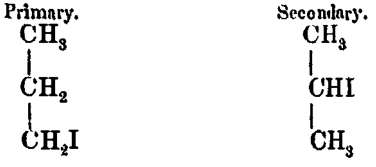
$$C_6H_5.C_2H_5$$



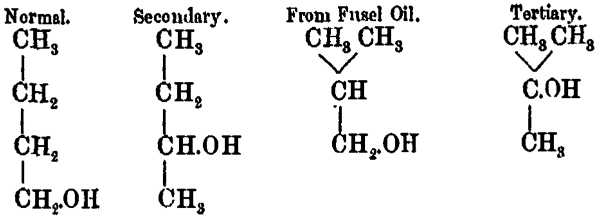
$$C_6H_4\left\{\begin{array}{l}CH_3\\CH_3\end{array}\right.$$

It has already been pointed out that all other carbon compounds may be regarded as derivatives of hydrocarbons, simple or compound radicals taking the place of hydrogen. By such substitutions, however, one and the same radical may replace hydrogen in different positions, and thus the number of possible isomeric carbon compounds is very large. The following examples represent some of the simpler cases :—

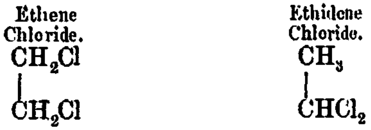
PROPYL IODIDE C_3H_7I.



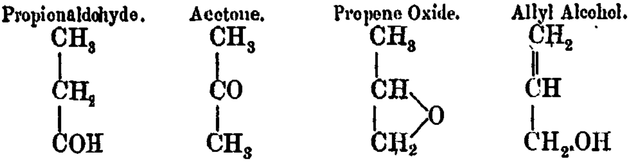
BUTYL ALCOHOL.



$C_2H_4Cl_2$



C_3H_6O



(2) *Metamerism.*—Compounds having the same composition and the same molecular weight, may also be formed by different radicals being linked together by the same polygenic element. Of such bodies, which are called *metameric compounds*, a very large number are known. In ammonia, for instance, one atom of hydrogen after the other may be replaced by alcohol radicals, and thus we are acquainted with the following metameric amines having the empirical formula C_3H_9N:—

Propylamine.	Methyl-Ethylamine.	Trimethylamine.
$N\begin{cases}C_3H_7\\H\\H\end{cases}$	$N\begin{cases}CH_3\\C_2H_5\\H\end{cases}$	$N\begin{cases}CH_3\\CH_3\\CH_3\end{cases}$

By introducing an alcohol radical in the place of hydrogen in the hydroxyl of an alcohol, ethers are obtained, which are metameric with other ethers as well as with an alcohol, as the following example shows:—

EMPIRICAL FORMULA $C_6H_{14}O$.

Hexyl Alcohol.	Methyl-Pentyl Ether.	Ethyl-Butyl Ether.	Dipropyl Ether.
$\left.\begin{matrix}C_6H_{13}\\H\end{matrix}\right\}O$	$\left.\begin{matrix}CH_3\\C_5H_{11}\end{matrix}\right\}O$	$\left.\begin{matrix}C_2H_5\\C_4H_9\end{matrix}\right\}O$	$\left.\begin{matrix}C_3H_7\\C_3H_7\end{matrix}\right\}O$

A very large number of metamerides are found amongst the ethers of the monobasic acids.

EMPIRICAL FORMULA $C_6H_{12}O_2$.

Caproic Acid.	Methyl Pentylate.	Ethyl Butyrate.	Propyl Propionate.
$\left.\begin{matrix}C_6H_{11}O\\ H\end{matrix}\right\}O$	$\left.\begin{matrix}C_5H_9O\\ CH_3\end{matrix}\right\}O$	$\left.\begin{matrix}C_4H_7O\\ C_2H_5\end{matrix}\right\}O$	$\left.\begin{matrix}C_3H_5O\\ C_3H_7\end{matrix}\right\}O$

Butyl Acetate.	Pentyl Formiate.
$\left.\begin{matrix}C_2H_3O\\ C_4H_9\end{matrix}\right\}O$	$\left.\begin{matrix}CHO\\ C_5H_{11}\end{matrix}\right\}O$

(3) *Polymerism.*—Compounds having the same percentage composition, but different molecular weights, are *polymeric.* A very striking example of polymeric compounds is furnished by the hydrocarbons of the general formula C_nH_{2n}.

Ethene	C_2H_4	Pentene . . .	C_5H_{10}
Propene	C_3H_6	Hexene . . .	C_6H_{12}
Butene	C_4H_8	Heptene . . .	C_7H_{14}

The following compounds are also polymeric:—

Acetylene . . .	C_2H_2	Formaldehyde.	CH_2O
Benzene	C_6H_6	Acetic Acid .	$C_2H_4O_2$
Styrolene . . .	C_8H_8	Lactic Acid .	$C_3H_6O_3$
Hydronaphthalene	$C_{10}H_{10}$	Grape Sugar .	$C_6H_{12}O_6$

PHYSICAL PROPERTIES OF THE CARBON COMPOUNDS.

Specific Gravity.—It has been already pointed out that the *specific gravity of gaseous compounds, or their vapour density, is equal to half their molecular weight; equal volumes of different gases contain the same number of molecules, or all gases have the same specific volume.*

Amongst liquid carbon compounds also, simple relations between their specific gravity on the one hand, and their molecular weight and chemical constitution on the other, have been found to exist. These relations are most clearly recognized by comparing the specific volume of liquids. To find the specific volume of a liquid we divide the molecular weight by the specific gravity. But as the specific weight changes with the temperature, it is obvious that such a comparison of specific volumes cannot be made at any arbitrary temperature, and it has been found that they are only comparable at a temperature at which their vapours have the same tension, as for instance at their boiling-points.

Ethyl alcohol boils at 78·4°, and has at this temperature the specific gravity 0·7360; its specific volume is therefore:—

$$\frac{46}{0{\cdot}7360} = 62{\cdot}5$$

Which means that 46 grams of alcohol have at 78·4° a volume of 62·5 cb. cm.

By comparing the specific volume of different liquids, the following laws have been found:—

(1) The difference of CH_2 in homologous series corresponds to a difference of 22 in the specific volume:—

	Molecular Weight.	Specific Volume.	Difference.
Formic Acid	46	42	—
Acetic Acid	60	64	22
Propionic Acid	74	86	22
Butyric Acid	88	108	22
Valeric Acid	102	130	22

From this it follows that the group CH_2 has the specific volume 22.

(2) Compounds containing as many times two atoms of hydrogen less, as others contain one atom of carbon more, have the same specific volume or the specific volume of one atom of carbon is equal to that of two atoms of hydrogen:—

		Molecular Weight.	Specific Volume.
Octane	C_8H_{18}	114	187
Cymene	$C_{10}H_{14}$	134	187
Ethyl Ether	$C_4H_{10}O$	74	106 8
Phenol	C_6H_6O	94	106 8

Now as the specific volume of CH_2 is 22, and that of hydrogen half that of carbon, it follows that the specific volume of carbon is 11, and that of hydrogen 5·5.

(3) Isomeric and metameric compounds have generally the same specific volume; amongst the exceptions we find a number of oxygen compounds. Whilst, therefore, the specific volumes of carbon and hydrogen remain the same, that of oxygen varies. This variation depends on the manner in which the oxygen is combined with the carbon. *When one atom of oxygen is linked to the carbon atom* by one combining unit only, its specific volume is 7·8; but when combined to carbon by both units its specific volume becomes 12·2. The specific volume of dyad sulphur varies also: when united with one combining unit it is 23, but when with both it is 28·6.

The specific volume of nitrogen in the amines is 2·3, in cyanogen compounds 17, and in nitroxyl NO_2 17·4. The specific volumes of the monad elements of the chlorine group do not exhibit such variations. They are Cl = 22·8. Br = 27·8. I = 37·5.

By means of these numbers the specific gravity of a liquid carbon compound can easily be calculated. The following table shows how near these calculated numbers agree with those deduced from the specific gravity:—

SPECIFIC VOLUME AT THE BOILING POINT.

		Found.	Calculated.	
Water	H_2O	18·8	$2 \times 5{\cdot}5 + 7{\cdot}8$	= 18·8
Formic Acid	$COH.OH$	41·8	$11 + 2 \times 5{\cdot}5 + 7{\cdot}8 + 12{\cdot}2$	= 42·0
Ethyl Alcohol	$C_2H_5.OH$	62·5	$2 \times 11 + 6 \times 5{\cdot}5 + 7{\cdot}8$	= 62·8
Acetone	$CO(CH_3)_2$	77·6	$3 \times 11 + 6 \times 5{\cdot}5 + 12{\cdot}2$	= 78·2
Mercaptan	$C_2H_5.SH$	76·1	$2 \times 11 + 6 \times 5{\cdot}5 + 23$	= 78·0
Aniline	$C_6H_5.NH_2$	106·8	$6 \times 11 + 7 \times 5{\cdot}5 + 2{\cdot}3$	= 106·8
Acetonitrile	$C_2H_5.CN$	77·2	$3 \times 11 + 5 \times 5{\cdot}5 + 17$	= 77·5
Ethyl Nitrate	$C_2H_5NO_3$	90·1	$\left\{\begin{array}{l} 2 \times 11 + 5 \times 5{\cdot}5 + 3 \\ \times 7{\cdot}8 + 17{\cdot}4 \end{array}\right\}$	= 90·3
Chloroform	$CHCl_3$	84·8	$11 + 5{\cdot}5 + 3 \times 22{\cdot}8$	= 84·9
Bromine	Br	28·1		= 27·8
Ethene Bromide	$C_2H_4Br_2$	99·0	$2 \times 11 + 4 \times 5{\cdot}5 + 27{\cdot}8$	= 99·6
Ethyl Iodide	C_2H_5I	86·4	$2 \times 11 + 5 \times 5{\cdot}5 + 37{\cdot}5$	= 87·0

There exist also certain relations between the specific gravity and the molecular weights of solids, but only a few carbon compounds have been studied as yet in this direction.

Melting Point and Boiling Point.—The number of carbon compounds which are gaseous at the ordinary temperature is very limited, most of them being liquids or solids. A great number of solids melt on heating, and most of the liquids boil and volatilize; but there exist also many which undergo a chemical change by the action of heat, decomposition taking place and the molecule being broken up, with the formation of a smaller or larger number of new compounds.

Generally speaking a body is the more volatile the more simple the constitution of the molecule, and the more complicated the latter is, the more liable is the compound to be decomposed by heat. Thus formaldehyde CH_2O is a gas; of its polymerides acetic acid $C_2H_4O_2$ boils at 118°, lactic acid $C_3H_6O_3$ volatilizes at 200°, but at the same time a large proportion undergoes decomposition, whilst grape sugar $C_6H_{12}O_6$ is not volatile at all, but is completely destroyed at a high temperature.

The more volatile a substance is the more simple is its constitution, from which follows that, in homologous series, the boiling-point must rise with every increase of CH_2; in some cases this increase is very regular, although different in different series, as the following examples show :—

NORMAL ALCOHOLS.

		Observed.	Calculated.	Difference.
Ethyl	C_2H_6O	78·4°	78·4°	—
Propyl	C_3H_8O	97	97	19°
Butyl	$C_4H_{10}O$	116	116	19
Pentyl	$C_5H_{12}O$	137	135	19
Hexyl	$C_6H_{14}O$	156·6	154	19
Heptyl	$C_7H_{16}O$	—	173	19
Octyl	$C_8H_{18}O$	192	192	19

In the series of the normal fatty acids the difference between the boiling-points of the lower members is also constant, being 22°, but afterwards it becomes less:—

NORMAL FATTY ACIDS.

		Observed.	Calculated.	Difference.
Acetic	$C_2H_4O_2$	118°	118°	—
Propionic	$C_3H_6O_2$	140·6	140	22°
Butyric	$C_4H_8O_2$	163·2	162	22
Pentylic	$C_5H_{10}O_2$	184·5	184	22
Hexylic	$C_6H_{12}O_2$	204·5	206	22
Heptylic	$C_7H_{14}O_2$	220	—	—
Octylic	$C_8H_{16}O_2$	233	—	—
Nonylic	$C_9H_{18}O_2$	254	—	—

In other cases, however, the difference between the boiling-points of the lower members of a series is not the same. Thus in the series of the normal paraffins it decreases regularly by about 4°, until it becomes a constant difference of 19°:—

		Boiling-points.		
		Found (mean).	Calculated.	Difference.
Methane	$C\ H_4$	—	—	—
Ethane	$C_2\ H_6$	—	—	—
Propane	$C_3\ H_8$	—	—	—
Butane	$C_4\ H_{10}$	1°	1°	—
Pentane	$C_5\ H_{12}$	38	38	37°
Hexane	$C_6\ H_{14}$	70	71	33
Heptane	$C_7\ H_{16}$	99	100	29
Octane	$C_8\ H_{18}$	124	125	25
Dodecane	$C_{12}H_{26}$	202	201	4 × 19
Hecdecane	$C_{16}H_{34}$	278	278	4 × 19

In the haloïd-ethers of the alcohol radicals and their acetates, the decrease appears to be about 2°:—

NORMAL IODIDES.

		Boiling-points.		
		Observed.	Calculated.	Difference.
Methyl	$C\ H_3\ I$	40°	40°	—
Ethyl	$C_2H_5\ I$	72	72	32°
Propyl	$C_3H_7\ I$	102	102	30
Butyl	$C_4H_9\ I$	129·6	130	28
Pentyl	$C_5H_{11}I$	155·4	156	26
Hexyl	$C_6H_{13}I$	179·5	180	24
Heptyl	$C_7H_{15}I$	—	202	22
Octyl	$C_8H_{17}I$	221	222	20

NORMAL BROMIDES.

		Observed.	Calculated.	Difference.
Ethyl	$C_2H_5\,Br$	39°	39°	—
Propyl	$C_3H_7\,Br$	71	71	32°
Butyl	$C_4H_9\,Br$	100·4	101	30
Pentyl	$C_5H_{11}Br$	128·7	129	28
Hexyl	$C_6H_{13}Br$	—	155	26
Heptyl	$C_7H_{15}Br$	—	179	24
Octyl	$C_8H_{17}Br$	199	201	22

NORMAL CHLORIDES.

		Observed.	Calculated.	Difference.
Ethyl	$C_2H_5\,Cl$	12·5°	13°	—
Propyl	$C_3H_7\,Cl$	46·4	46	33°
Butyl	$C_4H_9\,Cl$	77·6	77	31
Pentyl	$C_5H_{11}Cl$	105·6	106	29
Hexyl	$C_6H_{13}Cl$	—	133	27
Heptyl	$C_7H_{15}Cl$	—	158	25
Octyl	$C_8H_{17}Cl$	180	181	23

NORMAL ACETATES.

		Observed.	Calculated.	Difference.
Ethyl	$C_4\,H_8\,O_2$	74°	74°	—
Propyl	$C_5\,H_{10}O_2$	102	101	27°
Butyl	$C_6\,H_{12}O_2$	125·1	126	25
Pentyl	$C_7\,H_{14}O_2$	148·4	149	23
Hexyl	$C_8\,H_{16}O_2$	168·7	170	21
Heptyl	$C_9\,H_{18}O_2$	—	189	19
Octyl	$C_{10}H_{20}O_2$	207	208	19

It is generally stated, that metameric compounds, having an analogous constitution, boil at the same temperature, but, as the following examples show, this is not always the case:—

Formula $C_6H_{12}O_2$.	Boiling-point.	Formula $C_7H_{14}O_2$.	Boiling-point.
Butyl Acetate	124·3°	Pentyl Acetate	148·4°
Propyl Propionate	122·4	Butyl Propionate	146·0
Ethyl Butyrate	121·0	Propyl Butyrate	143·4

Isomeric compounds boil at different temperatures, the boiling-point being higher the more simple the constitution of the compound:—

		Boiling-point.
Hexane	C_6H_{14}	69·5°
Dimethyl-ethyl-methane	$CH\left\{\begin{matrix}(CH_3)_2\\ C_2H_5\end{matrix}\right.$	62
Tetramethyl-ethane	$C_2H_2(CH_3)_4$	58
Trimethyl-ethyl-methane	$C\left\{\begin{matrix}(CH_3)_3\\ C_2H_5\end{matrix}\right.$	45

		Boiling-point.
Propyl-benzene	$C_6H_5.C_3H_7$	153
Ethyl-methyl-benzene	$C_6H_4\left\{\begin{matrix}C_2H_5\\CH_3\end{matrix}\right.$	159
Trimethyl-benzene	$C_6H_4(CH_3)_3$	166
Normal Butyl Alcohol	$C_4H_9.OH$	116
Isobutyl Alcohol	$C_2H_3(CH_3)_2OH$	108
Secondary Butyl Alcohol	$\left.\begin{matrix}CH_3\\C_2H_5\end{matrix}\right\}CH.OH$	96
Tertiary Butyl Alcohol	$C(CH_3)_3OH$	82

By the subtraction of hydrogen the boiling-point is generally raised :—

Heptane.	Heptene.	Heptine.
C_7H_{16}	C_7H_{14}	C_7H_{12}
99°	100°	107°
Anthracene.	**Dihydroanthracene.**	**Hexhydroanthracene.**
$C_{14}H_{10}$	$C_{14}H_{12}$	$C_{14}H_{16}$
above 360°	305°	290°

Hydrocarbons always boil at a lower temperature than their derivatives, and the boiling-points of the latter rise when more hydrogen is displaced :—

Ethane.	Ethylamine.	Ethyl Chloride.
C_2H_6	$C_2H_5.NH_2$	C_2H_5Cl
gas	18·5°	12°
Ethyl Alcohol.	**Ethene Chloride.**	**Ethene Alcohol.**
$C_2H_5.OH$	$C_2H_4Cl_2$	$C_2H_4(OH)_2$
78·4°	82·5°	197·5°

Acetic Acid.	Chloracetic Acid.
$C_2H_3O.OH$	$C_2H_2ClO.OH$
118°	186°

Benzene.	Aniline.	Chlorobenzene	Phenol.
C_6H_6	$C_6H_5.NH_2$	C_6H_5Cl	$C_6H_5.OH$
82°	182°	135°	184°
Nitrobenzene.	**Dichlorobenzene.**	**Trichlorobenzene.**	**Diamidobenzene.**
$C_6H_5.NO_3$	$C_6H_4Cl_2$	$C_6H_3Cl_3$	$C_6H_4(NH_2)_2$
205°	172°	210°	287°

Optical Properties.—When a ray of light passes from one medium into another, it is, as is well known, bent or refracted. This refraction is very different for different media, but for the same two media the ratio between the sine of the angle of incidence and that of the angle of refraction is constant. Calling the angle of incidence i, and that of refraction r, this law is expressed by—

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

The value of n is called the index of refraction, and by speaking of the index of refraction of a body, we mean generally, the ratio existing between the sines of the two angles, when a ray enters the body from the air. The index of refraction changes with the temperature as well as with the specific gravity (d) in such a way that the value $\frac{n-1}{d}$, called the specific refractive energy, remains constant. By multiplying this value by the molecular weight of the substance, we obtain its molecular refractive energy, which depends on the chemical composition. The relations existing between the molecular refractive energy and the chemical composition have been best studied for the liquid compounds belonging to the group of fatty substances, and the non-saturated compounds associated with them.

The following are the most important results :—

(1) Isomerides and metamerides have the same molecular refractive energy.

(2) The molecular refractive energy increases in homologous series 7·6, for each increase of CH_2.

(3) By the addition of two atoms of hydrogen the molecular refractive energy increases 2·6.

(4) The refractive molecular energy of the acids of the series $C_nH_{2n}O_2$ is equal to $7{\cdot}6n + 6$.

From these results we can calculate the atomic refractive energy of carbon, hydrogen, and oxygen; we find that in these liquid compounds these elements have the following refractive energies :—

Carbon	5
Hydrogen	1·3
Oxygen	3

By means of these members the molecular refractive energy of a liquid of known composition can easily be calculated. The following example shows how well the value thus obtained agrees with that found by means of the observed index of refraction. To find the latter, a hollow prism consisting of glass plates was filled with the liquid, and by means of it, the deviation of the yellow sodium line observed; the temperature being 20°.

Ethyl Alcohol C_2H_6O. $d = 0{\cdot}7964$ $n = 1{\cdot}3606$

$$\frac{n-1}{d} = 0{\cdot}4528.$$

By multiplying the latter number by 46, the molecular weight of alcohol, we obtain the molecular refractive energy = 20·8, whilst calculating it from the chemical formula we have—

$$2 \times 5 + 6 \times 1{\cdot}3 + 3 = 20{\cdot}8.$$

Acetic Acid $C_2H_4O_2$. $d = 1{\cdot}053$. $n = 1{\cdot}372$.

$$\frac{n-1}{d} = 0{\cdot}3533. \qquad 60 \times 0{\cdot}3533 = 21{\cdot}2.$$

Calculated from the composition—

$$2 \times 5 + 4 \times 1{\cdot}3 + 2 \times 3 = 21{\cdot}2.$$

Ethyl Acetate $C_4H_8O_2$. $d = 0{\cdot}8977$. $n = 1{\cdot}3715$.

$$\frac{n-1}{d} = 0{\cdot}4138. \qquad 88 \times 0{\cdot}4138 = 36{\cdot}4.$$

Butyric Acid $C_4H_8O_2$. $d = 0{\cdot}9608$. $n = 1{\cdot}3973$.

$$\frac{n-1}{d} = 0{\cdot}4135. \qquad 88 \times 0{\cdot}4135 = 36{\cdot}4.$$

The two latter compounds are metameric, and have therefore the same specific and molecular refractive energy, which latter found by calculation is—

$$4 \times 5 + 8 \times 1{\cdot}3 + 2 \times 3 = 36{\cdot}4.$$

The specific refractive power of mixtures is the mean of that of their constituents, and if we know what compounds are present in a mixture of liquids, we are able to find by means of this optical analysis the quantity of each, which by chemical analysis can only be done when the composition of the two bodies is widely different. It often happens that such mixtures containing two alcohols, or two hydrocarbons, &c., cannot be completely separated, either by chemical or by physical means, but yet by means of an optical analysis we can find the quantity of each.

Mixture of Ethyl Alcohol, and Water.

	$\frac{n-1}{d}$
Ethyl Alcohol	0·4528
Water	0·3324
Mixture	0·4225

Calling the quantity of alcohol contained in 100 parts x, and that of the water y, we have the simultaneous equations—

(1) $x + y = 100$.
(2) $0{\cdot}4528x + 0{\cdot}3324y = 0{\cdot}4225 \times 100$.

From this we find—

$$\begin{array}{r} x = 74{\cdot}84 \\ y = 25{\cdot}16 \\ \hline 100{\cdot}00 \end{array}$$

which agrees as nearly as possible with the real composition—

Alcohol	74·9
Water	25·1
	100·0

Mixture of Ethyl Alcohol and Amyl Alcohol.

	$\frac{n-1}{d}$
Ethyl Alcohol	0·4528
Amyl Alcohol	0·5033
Mixture	0·4940

$$\begin{aligned}&(1)\ x + y = 100\\&(2)\ 0{\cdot}4528x + 0{\cdot}5033y = 49{\cdot}4\end{aligned}$$

$$\begin{aligned}y &= 81{\cdot}5\\x &= 18{\cdot}4\end{aligned}$$

The liquid being prepared by mixing together—

Amyl Alcohol	81·3
Ethyl Alcohol	18·7

Not only the composition of mixtures, but also that of compounds can be ascertained by means of the optical analysis. As this method, however, depends entirely on the exact determination of the specific refractive energy of the elements, and as that of oxygen is not yet accurately known, reliable results have been only obtained in the analysis of hydrocarbons. Thus the composition of amylene C_5H_{10} was found from the following data:—

$$d = 0{\cdot}6733. \qquad n = 1{\cdot}3706. \qquad \frac{n-1}{d} = 0{\cdot}5504.$$

The value of $\frac{n-1}{d}$ for carbon is $\frac{5}{12}$, or more exactly 0·4220, and that of hydrogen 1·3016. Calling the percentage of carbon y, and that of hydrogen x, we have the equations:—

$$\begin{aligned}&(1)\ x + y = 100\\&(2)\ 0{\cdot}422y + 1{\cdot}3016x = 55{\cdot}04\end{aligned}$$

$$x = 14{\cdot}6. \qquad y = 85{\cdot}4.$$

Calculated composition of C_5H_{10}.		Found.
Carbon	85·7	85·4
Hydrogen	14·3	14·6

Similar relations between refractive energy and composition are exhibited by liquid carbon compounds belonging to the aromatic group and other groups richer in carbon, but they have not yet been so completely investigated. As yet it has only been shown that their molecular refractive energies are higher than those calculated from the values given above, and the higher they are, the more compactly the carbon atoms are linked together.

Circular Polarization.—Those carbon compounds which possess the power of turning the plane of polarized light are either a product of life, or derivatives of such bodies; no carbon compound prepared by synthesis has been found to be optically active. Solid optically active compounds form crystals generally having hemihedral faces, and often exist in two modifications, one turning the polarized ray to the right, and the other to the left. In such a case the hemihedral faces are differently arranged, and when the two kinds of crystals are placed in the *same position it will be found that the hemihedral faces appear* in one crystal on the right, and in the other on the left side, or one of the crystals looks like the image of the other in a mirror. These bodies are not only optically active in the solid state, but also in solution; and there exist also many liquids having this property, as for instance, amyl alcohol, oil of turpentine, &c.

This optical property has been made use of in the arts; it is used to determine the quantity of sugar contained in syrups. Under the head of cane-sugar it will be explained how, by simply measuring the angle of deviation, the quantity of sugar contained in a liquid can be ascertained.

Colour of the Carbon Compounds.—Most carbon compounds are colourless, when in the pure state; but there exist also a great number having characteristic colours, and many of these are used as dye stuffs or for the preparation of pigments, such as indigo, the colours of madder-root, cochineal, aniline colours, &c. It appears that the colour of these bodies depends on their chemical constitution; they contain certain elements, as oxygen and nitrogen, combined in a peculiar manner, as we shall see when we come to the study of these bodies.

Odour and Taste.—The odours of volatile carbon compounds vary very much, as the following examples show: spirits of wine, ether, acetic ether, acetic acid, chloroform, camphor, oil of cloves, &c. Compounds having a similar constitution often possess a similar smell. Thus the marsh-gas hydrocarbons all possess a faint smell of flowers, which is more or less perceptible according to the volatility of the body. The compound ethers of the fatty acids smell like various kinds of fruit, and are on that account used by confectioners and perfumers. Most sulphur compounds, in which this element is not combined with oxygen, are characterized by their disagreeable odour, and many chlorides have a smell similar to that of chloroform.

Relations between odour and chemical constitution certainly exist; but only a few such are known. Thus the amines or compound ammonias have an odour resembling that of ammonia, and many aldehydes, compounds which readily absorb oxygen from the air, possess a peculiar suffocating smell.

The taste of carbon compounds is equally as varying as their odour; we find here also that analogous constitution produces a similar taste. The alkaloids, as quinine, strychnine, &c., have an intensely bitter taste, whilst the taste of the alcohols of polygenic radicals, as glycerin, mannite, and sugar, is pleasantly sweet.

Solubility.—A great number of carbon compounds are soluble in *water, others only in alcohol, ether, acetic acid, benzene, &c.* These different solvents are made use of in separating or purifying them. In homologous series the first members are generally more soluble in water than the higher ones. Thus in the series of the alcohols and fatty acids, the lower members are miscible with water in all proportions, whilst those following next dissolve only in certain proportions, and the highest are insoluble in water. All hydrocarbons are either very sparingly soluble, or quite insoluble in water; by replacing in them a part of the hydrogen by hydroxyl or oxygen, compounds are formed which are more soluble, generally in proportion to the more oxygen they contain. Thus butyl C_4H_{10} is almost insoluble in water, butyl alcohol $C_4H_9(OH)_2$ readily soluble, and butylene alcohol $C_4H_8(OH)$ mixes with water in all proportions. Succinic acid $C_4H_6O_4$ is more soluble than butyric acid $C_4H_8O_2$, and malic acid $C_4H_6O_5$ is very deliquescent.

FRACTIONAL DISTILLATION.

This is an operation often made use of in the preparation of pure carbon-compounds to isolate the different constituents contained in a mixture of volatile bodies. On subjecting a mixture of two liquids to distillation, at the beginning a large proportion of the more volatile body comes over; but the boiling-point rises continually, and more and more of the vapour of the less volatile compound mixes with that of the more volatile. It is only when the difference between the boiling-points of the two bodies is very considerable that it is possible to effect an almost complete separation by one distillation. In this case, when the operation is carried on very slowly, the more volatile body distils at a nearly constant temperature; and as soon as all of it has passed over, the thermometer rises rapidly to the boiling-point of the less volatile compound. But in most cases it is impossible even to approach a separation by only one distillation. By collecting separately the portions distilling between certain intervals of temperature, say between each 5°, or 10°, the first will consist chiefly of the lower boiling body, and the last of the less volatile substance; whilst the composition of the greatest portion boiling between these two approaches more or less to that of the original mixture.

The following example shows well how very imperfectly even bodies whose boiling-points are not close together are separated by one distillation. A mixture of 100 grams of ethyl alcohol (boiling-point 78·4°) and 100 grams of amyl alcohol (boiling-point 132°) was distilled from a long-necked flask, and the distillate collected in 7 fractions, the composition of which was found by optical analysis:—

Boiling-point	80°-90°	90°-100°	100°-110°	110°-120°	120°-130°	130°-131°	131°-132°
Weight of fraction . . .	47	45	25	14	18	11	36
Per cent. of Ethyl Alcohol	88·1	83	61·5	52·1	18·4	4·5	0·2
Per cent. of Amyl Alcohol	19·0	18	38·5	47·0	81·6	95·5	99·8
	100·0	100	100·0	100·0	100·0	100·0	100·0

In the flask remained 4 grams of pure amyl alcohol.

It is easy to understand the reason why, in such a distillation, the less volatile body distils so much below its boiling-point. As is well known, all volatile bodies evaporate below their boiling-points, and this takes place with greater facility when the tension of the vapour is higher, and the quicker the surrounding atmosphere is changed. Now these very conditions are fulfilled on boiling a mixture of two liquids; the vapour of the lower boiling body carries that of the less volatile substance with it on passing through the mixture, and being quickly condensed, a new atmosphere is continually formed.

In most cases such mixtures contain more than two compounds; thus the so-called fusel oil is a mixture of several homologous alcohols, and American petroleum contains a large number of marsh gas hydrocarbons, whilst the light oils of coal-tar contain benzene and homologous hydrocarbons. In order to isolate from such mixtures tolerably pure compounds, the different fractions obtained in the first distillation are again submitted to the same operation, and those portions which distil between the same intervals of temperature collected separately; and this process is repeated until bodies with a nearly constant boiling-point have been obtained.

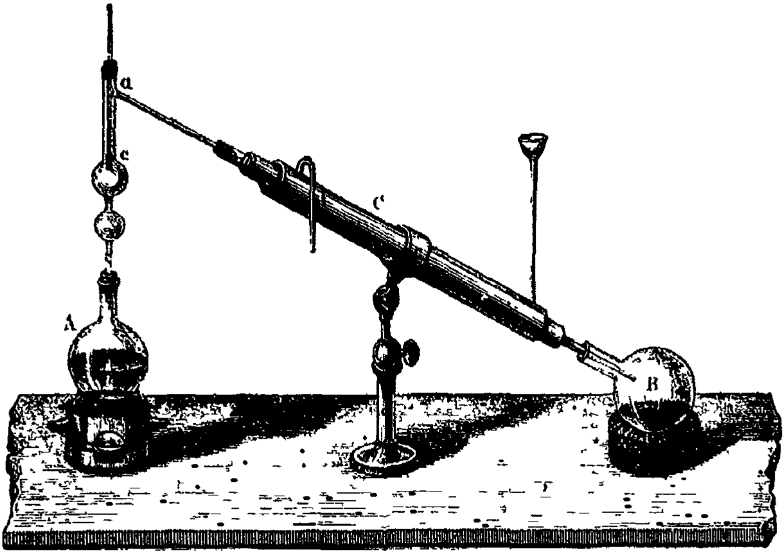


Fig. 7.

A complete separation cannot be effected in this way; since substances obtained by this method, though having a constant boiling-point, are never quite pure, and thus require to be further treated in different ways in order to effect a complete separation.

The apparatus used in the laboratory for fractional distillation is seen in Fig. 7. The boiling liquid is contained in a flask, A, the vapours enter the bulb tube C, containing the thermometer; the large surface allows the less volatile substance to condense, whilst the more volatile vapours enter the condenser, round which cold water flows. By such an arrangement the number of distillations required is much diminished.

CLASSIFICATION OF THE CARBON COMPOUNDS.

It has already been fully explained that the carbon compounds are divided into several large groups, according to the manner in which the carbon atoms are linked together; each of these may again be subdivided into compounds of monad, dyad, triad, &c., radicals. It is, however, at present impossible to arrange all carbon compounds according to such a system, because several of these groups have been very incompletely studied, and there exists a very large number of organic bodies the constitution of which is not known at all. We shall therefore arrange the carbon compounds in the following order.

(1) The oxides and the sulphide of carbon, as well as the cyanogen compounds, exhibit in their behaviour more resemblance to the compounds of the other elements than the remainder of the carbon compounds, and for this reason they are generally treated of under the head of inorganic chemistry.

We shall consider these compounds first, as the radicals contained in these occur also in a large number of other carbon compounds, the chemical constitution of which will be only properly understood by being well acquainted with that of the former.

(2) The large group of fatty substances coming next has been very fully investigated; they are subdivided again according to the quantivalence of their radicals. Much less complete, however, is our knowledge of the non-saturated compounds. As most of them are very nearly connected with compounds of the fatty group, being either obtained from the latter, or transformed into such by the addition of hydrogen, they will be considered along with them.

(3) Next come the compounds which are richer in carbon than the fatty substances, and which are not converted into such by the addition of hydrogen. These are again subdivided into several groups, amongst which that of the aromatic compounds has been most fully investigated. They are so arranged that all the compounds containing the same number of carbon atoms in the molecule are placed together.

The last group consists of a number of compounds existing in plants and animals, the constitution of which is not yet known. Most of them have a very complicated constitution, and exhibit only a few relations to compounds of known structure.

CYANOGEN COMPOUNDS.

Carbon and nitrogen do not combine directly; but when nitrogen is passed over a white-hot mixture of charcoal and an alkali or an alkaline carbonate, combination takes place, and a metallic cyanide is formed:—

$$N_2 + C_4 + K_2CO_3 = 2KCN + 3CO$$
$$N_2 + C_3 + BaO = Ba(CN)_2 + CO$$

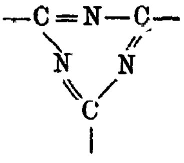
Cyanides are formed much more abundantly when nitrogenous carbon compounds are heated with alkalis, and this is the principal method by which potassium cyanide is prepared on a large scale. This compound forms the starting point for the preparation of other cyanogen compounds, amongst which prussic acid, prussian blue, and prussiate of potash are best known. All these compounds contain the monad group CN, in which the three combining units of nitrogen are saturated with three of tetrad carbon; this radical has been called cyanogen (κυανός blue), and it is contained in a large number of compounds, of which the following are examples:—

Cyanogen Hydride	CNH	Cyanamide	$CN.NH_2$
Cyanogen Chloride	CNCl	Potassium Cyanide	CNK
Cyanogen Sulphide	$(CN)_2S$	Dicyanogen	CN CN
Cyanic Acid	CN.OH		

Besides these simple compounds we also know a number of polymeric modifications:—

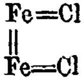
Cyanuric Chloride	$C_3N_3Cl_3$
Cyanuric Acid	$C_3N_3(OH)_3$
Cyanuric Amide	$C_3N_3(NH_2)_3$

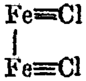
These compounds contain the triad radical C_3N_3, which has probably the following constitution:—



The metallic cyanides have a great tendency to unite with one another to form double cyanides; in some of these salts the heavy metal cannot be detected by the usual reagents; being contained in them in a mode of combination different from that exhibited in other salts. The most important of them are *Potassium Ferrocyanide* $Fe(CN)_6K_4$, and *Potassium Ferricyanide* $Fe(CN)_6K_3$.

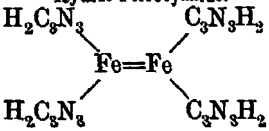
When these salts are acted upon by hydrochloric acid, the potassium is replaced by hydrogen, and the compounds *Hydric Ferrocyanide* $Fe(CN)_6H_4$ and *Hydric Ferricyanide* $Fe(CN)_6H_3$ are formed; both of which are powerful acids. The constitution of these compounds may be explained by means of the quantivalence of iron, which is a tetrad, and forms two series of compounds—ferrous compounds, which contain two atoms of iron as a tetrad group, and ferric compounds, in which two atoms of the metal are combined forming a hexad group, thus:—

Ferrous Chloride

$$\begin{array}{l} Fe{=}Cl \\ \| \\ Fe{=}Cl \end{array}$$

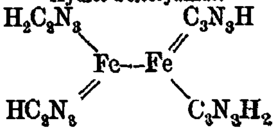
Ferric Chloride

$$\begin{array}{l} Fe{\equiv}Cl \\ | \\ Fe{\equiv}Cl \end{array}$$

If in ferrous chloride each atom of chlorine be replaced by the triad radical C_3N_3, the octad radical *Ferrocyanogen* is obtained, whilst the hexad radical *Ferricyanogen* is formed by $4\,C_3N_3$ combining with the hexad ferric group, thus:—

Hydric Ferrocyanide.

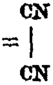


Hydric Ferricyanide.



The formulæ given above, and which are those generally used for their simplicity, represent, as we now see, only half a molecule.

CYANOGEN GAS OR DICYANOGEN $C_2N_2 =$


$$C_2N_2 = \begin{array}{c} CN \\ | \\ CN \end{array}$$

This gas, which occurs in small quantities in the gases of iron blast furnaces, is obtained by the action of heat on the cyanides of mercury, silver, or gold, and is best prepared by heating dry mercuric cyanide in a tube or retort of hard glass, and collecting the gas over mercury. It is colourless, has a pungent smell like prussic acid, and is poisonous. Cyanogen gas condenses to a liquid under a pressure of about 4 atmospheres, or by exposure to extreme cold under the ordinary pressure; it boils at – 21°, and solidifies at – 34° to a radiated icy mass. It burns with a beautiful purple flame, forming nitrogen and carbonic dioxide. Cold water absorbs 4—5 vol. of the gas, and it is also freely soluble in alcohol. These solutions soon assume a brown colour; after some time a brown powder is deposited, and the aqueous solution now contains carbon dioxide, ammonia, urea, and a large quantity of ammonium oxalate:—

$$C_2N_2 + 4H_2O = C_2O_4\,(NH_4)_2$$

When the gas is passed into strong hydrochloric acid, or when a small quantity of aldehyde is added to its aqueous solution, it takes up only 2 molecules of water, oxamide being formed:—

$$C_2N_2 + 2H_2O = C_2O_2(NH_2)_2$$

By the inverse reaction, that is by taking the elements of water out of ammonium oxalate and oxamide, which may be done by heating them with phosphorus pentoxide, cyanogen gas is again formed

Potassium combines directly with cyanogen gas under the influence of heat, and by passing the gas into potash solution or over red-hot potassium carbonate, a mixture of cyanide and cyanate is formed :—

$$C_2N_2 + K_2CO_3 = CNK + CNOK + CO_2$$

In the preparation of cyanogen a brown powder is left behind which is a polymeric modification of the gas, and is called *para-cyanogen.* By continued application of heat this body is completely transformed into gaseous cyanogen.

HYDROGEN CYANIDE, HYDROCYANIC OR PRUSSIC ACID CNH.

This compound is formed by replacing the metal in metallic cyanides by hydrogen, and may be obtained by acting on potassium cyanide with a dilute acid, or by decomposing mercuric cyanide with hydrogen sulphide. It is, however, best prepared by heating a mixture of 10 parts of coarsely powdered potassium ferrocyanide with a perfectly cold mixture of 7 parts of sulphuric acid with (according to the strength of the prussic acid required) 14—40 parts of water. The flask must be connected with a good condenser, the lower end of which dips under water contained in a receiver. To prepare the anhydrous acid, the sulphuric acid is diluted with twice its weight of water, and the vapour after having passed a U tube which is filled with calcium chloride, and immersed in water of 30°, is condensed in a vessel surrounded by a freezing mixture.

Pure hydrocyanic acid is a colourless liquid, boiling at 26·5°, and solidifying at – 15° to a mass like ice. It is excessively poisonous, a drop producing instant death when swallowed, and the inhalation of its vapour is likewise instantly fatal. It has a peculiar odour, and its vapour when diluted with air produces, when inhaled, a peculiar irritation in the throat. It dissolves in water, alcohol, and ether, in all proportions, and is, as well as its concentrated aqueous solution, inflammable, burning with a purple flame.

The anhydrous acid soon undergoes spontaneous decomposition; giving off ammonia, and leaving a brown residue. It suffers the same decomposition in an aqueous solution, a part, however, being converted into ammonium formate. This decomposition is almost entirely prevented by the presence of a small quantity of formic or a mineral acid; but when it is mixed with strong acids, water is taken up, and ammonia and formic acid are produced. On the other hand, when ammonium formate is heated, it splits up into water and prussic acid:—

$$NH_4CO_2H = 2H_2O + NCH$$

Hydrocyanic acid is also formed by passing the electric discharge through a mixture of acetylene and nitrogen, thus :—

$$C_2H_2 + N_2 = 2NCH$$

Hydrocyanic acid is used as a medicine, and is contained in certain officinal preparations such as laurel water, bitter almond water, &c., which are obtained by distilling the leaves of the common laurel, or bitter almonds with water. These plants do not contain the prussic acid ready formed; but, in common with most of the plants of the same family, contain *amygdalin,* a complicated compound which, under certain circumstances, splits up into sugar, oil of bitter almonds, and prussic acid.

To estimate the quantity contained in these preparations, to a measured or weighed quantity an excess of potash solution is added, and then by means of a burette a solution of silver nitrate containing 6·3 grams in one litre. The silver solution is added, until a permanent precipitate appears; each cb.cm. corresponds to two milligrams of anhydrous prussic acid. In this reaction the double cyanide $AgCN + KCN$ is formed, which is not decomposed by alkalis, and is soluble in water; but as soon as exactly half the quantity of prussic acid present is converted into silver cyanide, one drop more of the silver solution will produce a permanent precipitate of silver cyanide.

To detect hydrocyanic acid, as in cases of poisoning, the suspected matter is acidulated with tartaric acid, and the prussic acid distilled off by means of a water bath. The distillate is made alkaline with caustic soda, and a mixture of a ferrous and ferric salt (a solution of ferrous sulphate oxidised by exposure to the air) is added, and then an excess of hydrochloric acid; prussian blue remains undissolved if prussic acid is present; if the quantity contained is very small, the solution appears first of a green colour, and on standing deposits dark blue flakes. When dilute prussic acid is mixed with *yellow* ammonium sulphide, and the liquid evaporated over a water bath, ammonium sulphocyanate is formed; the presence of this body is made known by means of ferric chloride, which produces a deep blood-red coloration.

METALLIC CYANIDES.

Potassium Cyanide KCN.—The different modes of formation of this salt have already been mentioned; it is often produced in large quantities in the blast furnaces in which iron ores are smelted with coke or coal. Pure potassium cyanide is obtained by passing the vapour of prussic acid into an alcoholic solution of potash; the salt, being but slightly soluble in alcohol, crystallizes out in cubes. The pure compound is also formed by the ignition of potassium ferrocyanide, which is decomposed at a red heat into potassium cyanide, iron carbide, and nitrogen :—

$$Fe(CN)_6K_4 = 4KCN + FeC_2 + N_2$$

The commercial product is prepared by fusing the ferrocyanide with potassium carbonate:—

$$Fe(CN)_6K_4 + K_2CO_3 = 5KCN + KOCN + Fe + CO_2$$

On heating the mixture, carbon dioxide escapes, and the iron separates in the form of a spongy mass, from which the fused cyanide is poured off. The salt thus obtained is mixed with some cyanate, the presence of which, however, is of little or no consequence for most of the purposes for which potassium cyanide is used.

Potassium cyanide is largely used as a chemical reagent, in galvanic silvering and gilding, and in photography, &c. It is very soluble in water, sparingly in cold, more so in hot alcohol. At a red heat it fuses to a clear liquid, which slowly takes up oxygen from the air. This takes place more quickly in presence of metallic oxides, the cyanide being converted into the cyanate; on this account it is used as a reducing agent in blow-pipe experiments. On fusing it with sulphur, potassium sulphocyanide is formed, KSCN. Potassium cyanide is decomposed by the weakest acids, even by moist carbon dioxide; it therefore smells of prussic acid, and is as dangerous a poison.

Sodium Cyanide NaCN crystallizes likewise in cubes, and has the greatest resemblance to the potassium salt.

Ammonium Cyanide NH_4CN is formed by the direct union of ammonia and prussic acid, and can also be obtained by heating a mixture of sal-ammoniac and potassium cyanide in a retort connected with a well-cooled receiver. It crystallizes in cubes, smells strongly of ammonia and prussic acid, and boils at 36°. Its vapour is inflammable, and burns with a yellow flame. It is a very unstable compound, gradually changing into a brown matter, a decomposition which takes place more quickly in the moist state.

Silver Cyanide, AgCN.—Soluble cyanides produce in a solution of silver nitrate a white precipitate of silver cyanide, resembling silver chloride; it is insoluble in dilute nitric acid, but dissolves readily in ammonia and in potassium cyanide, from which solution the double salt, AgCN + KCN, can be obtained in octahedrons on evaporation. This salt is used for electro-silvering.

Zinc Cyanide, $Zn(CN)_2$ is obtained as a white precipitate by adding potassium cyanide to a solution of a zinc salt; it is soluble in an excess of potassium cyanide.

Nickel Cyanide $Ni(CN)_2$.—Nickel salts are precipitated by potassium cyanide; the apple-green precipitate produced is readily soluble in an excess of potassium cyanide solution, forming the double salt, $Ni(CN)_2 + 2KCN$; by adding hydrochloric acid to a solution of this salt, nickel cyanide is again precipitated.

Cobalt Cyanide $Co(CN)_2$ is a brownish red precipitate, which also dissolves easily in an excess of potassium cyanide. When this solution is slightly acidulated and boiled, hydrogen is given off, and potassium cobalticyanide is formed:—

$$2Co(CN)_2 + 6KCN + 2HCN = Co_2(C_3N_3)_4K_6 + H_2$$

The solution thus obtained is *not* precipitated by hydrochloric acid, and this reaction is therefore used for the separation of cobalt from nickel.

Mercuric Cyanide $Hg(CN)_2$ is obtained by dissolving mercuric oxide in aqueous prussic acid, or by boiling this oxide with prussian blue and water. It crystallizes in colourless, quadratic prisms, and is very poisonous.

Cyanides of Gold.—On precipitating a solution of gold trichloride with ammonia and dissolving the precipitate in a solution of potassium cyanide, the double salt $Au_2(CN)_2 + 2KCN$ is formed, which is used for electro-gilding. If a neutral solution of gold trichloride is added to a hot solution of potassium cyanide the salt $Au(CN)_3+KCN$ is formed, which crystallizes on cooling, forming colourless crystals.

Nitrocyanide of Titanium $Ti(CN)_2+3\ Ti_3N_2$.—This remarkable compound, which was formerly believed to be metallic titanium, occurs as a furnace product in the form of opaque copper-coloured cubes in iron blast furnaces.

The same compound is obtained by exposing a mixture of potassium ferrocyanide and titanic dioxide to a strong white heat. When this body is heated to redness in a current of steam, titanic dioxide is formed with the evolution of hydrogen, ammonia, and hydrocyanic acid:—

$$Ti(CN)_2 + 3Ti_3N_2 + 20H_2O = 10TiO_2 + 10H_2 + 2CNH + 6NH_3$$

FERROCYANIDES AND FERRICYANIDES.

The constitution of these compounds has already been discussed. Of the two isomeric radicals, $Fe_2(C_3N_3)_4$, *Ferrocyanogen* is an octad and *Ferricyanogen* a hexad. We shall, however, in the following pages use the simplest formulæ and express half the molecule of ferrocyanogen by Cfy, and half that of *Ferricyanogen* by Cfdy, whilst Fe will stand for ferrous and Fe_2 for ferric iron.

Potassium Ferrocyanide K_4Cfy can be obtained by mixing solutions of potassium cyanide and ferrous sulphate: a brown precipitate is first formed, $Fe_2(CN)_5K$, which dissolves in an excess of potassium cyanide, forming potassium ferrocyanide:—

$$Fe_2(CN)_5K + 7KCN = Fe_2(C_3N_3)_4K_8$$

This compound, commonly known by the name of *yellow prussiate of potash*, forms the starting point for preparing most of the other cyanogen compounds, and is prepared on the large scale by fusing together crude potashes, iron filings, and animal matter such as horns, hoofs, hair, blood, leather clippings, or the charcoal obtained from them.

The products formed are potassium cyanide, ferrous sulphide, and potassium-ferrous sulphide K_2S+FeS; the two latter originating from the sulphates contained in potashes, and the sulphur existing in the animal matter. By exhausting the melt with water, the following reaction sets in:—

$$6KCN + FeS = Fe(CN)_6K_4 + K_2S$$

By employing materials free from sulphur a greater yield of cyanide is obtained. Some manufacturers therefore use purified potashes and no iron, and add to the liquor, ferrous carbonate which has been freshly precipitated or finely powdered spathose iron:—

$$6KCN + FeCO_3 = Fe(CN)_6K_4 + CO_3K_2$$

Potassium ferrocyanide crystallizes from its concentrated solution in large yellow crystals, containing 3 mol. of water of crystallization, and belonging to the quadratic system (Fig. 8). It is readily soluble in water, and is not poisonous; when given in large doses it acts as a laxative. The crystals lose their water at 100°, and are converted into a white powder. Heated to a dull red heat it decomposes, potassium cyamide, iron carbide, and free nitrogen being formed. Ferrous salts produce in its solution a white precipitate, which when exposed to the air rapidly absorbs oxygen, and turns blue; ferric salts produce a deep blue precipitate having the composition $\left.\begin{matrix}Fe_2\\K_2\end{matrix}\right\}Cfy_2$; this compound is insoluble in salt solutions, but dissolves freely, and with a beautiful blue colour, in water; it loses its solubility on drying it at 110° when it loses water. Its aqueous solution is not changed by ferric salts, but on addition of ferrous sulphate a deep blue precipitate is formed, potassium being replaced by dyad iron:—

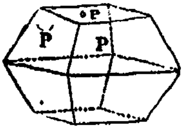


FIG. 8.

$$\left.\begin{matrix}Fe_2\\K_2\end{matrix}\right\}Cfy_2 + FeSO_4 = \left.\begin{matrix}Fe_2\\Fe\end{matrix}\right\}Cfy_2 + K_2SO_4$$

This compound is the chief constituent of *prussian blue*, which is obtained by precipitating prussiate of potash with commercial iron sulphate (a mixture of ferrous and ferric sulphates), and washing the precipitate with water in the presence of air or chlorine water, and treating it with dilute hydrochloric acid, in order to remove ferric oxide or basic iron salts. The commercial product always contains potassium, and appears to be a mixture of the two compounds described above. It forms blue masses having a conchoidal fracture and a coppery lustre. It is insoluble in acids with the exception of oxalic acid, which dissolves it with a fine blue colour; this solution is used as a blue ink. By alkalis it is decomposed, a ferrocyanide of the alkali-metal being formed.

Hydric Ferrocyanide or Hydroferrocyanic Acid $CfyH_4$.—On adding strong hydrochloric acid to a concentrated solution of potassium ferrocyanide, a white precipitate of hydric ferrocyanide is obtained, which is purified by pressing between blotting paper, dissolving in spirits of wine, and pouring on this solution a layer of ether; after some time the pure acid separates out in colourless crystals. On mixing the alcoholic solution with ether, the compound is precipitated as a crystalline powder. When exposed to the air, it absorbs oxygen; prussic acid is given off, and prussian blue formed; this change takes place more quickly on the application of heat. Hydric ferrocyanide is a strong acid which decomposes not only carbonates but also acetates and oxalates. On boiling its aqueous solution hydrocyanic acid is given off and a white precipitate of ferrous ferrocyanide $Fe_2Cfy = Fe_3(CN)_6$ is formed:—

$$3H_4(CN)_6 = 12HCN + Fe_3(CN)_6$$

This decomposition occurs in the preparation of prussic acid from potassium ferrocyanide and dilute sulphuric acid.

The ferrocyanides of other metals are either sparingly soluble in water or insoluble, and are therefore obtained as precipitates by adding a solution of potassium ferrocyanide to solutions of metallic salts; potassium ferrocyanide is for this reason used as a reagent. Thus with solutions of barium salts it gives a crystalline precipitate having the composition BaK_2Cfy, and by adding a solution of the ferrocyanide to a solution of copper sulphate, a red precipitate of copper ferrocyanide Cu_2Cfy is formed; whilst by adding a solution of a cupric salt to an excess of potassium ferrocyanide a brown precipitate CuK_2Cfy is obtained.

Potassium Ferricyanide K_3Cfdy.—This compound, commonly known as *red prussiate of potash*, is prepared by passing chlorine into a solution of potassium ferrocyanide:—

$$K_4(CN)_6Fe + Cl = KCl + K_3(CN)_6Fe$$

Potassium chloride and ferricyanide are formed and separated from one another by crystallization. The red prussiate crystallizes in large, dark red, monoclinic prisms, soluble in water with a brownish green colour. By reducing agents it is re-converted into a ferrocyanide; this is easily effected by adding potassium amalgam to its aqueous solution. Its alkaline solution is, therefore, a powerful oxidizing agent; it converts chromic oxide into chromic acid, and manganese monoxide into the dioxide:—

$$6K_3(CN)_6Fe + 10HOK + Cr_2O_3 = 6K_4(CN)_6Fe + 2K_2CrO_4 + 5H_2O$$

Ferric salts are not precipitated by the addition of potassium ferricyanide, the solution only assumes a dark brown colour; but with ferrous salts it produces a dark blue precipitate, called *Turnbull's blue*, which is generally considered to consist of *ferrous ferricyanide* $Fe_3(Cfdy)_2$. This precipitate, however, has the same composition and the same properties as the compound $\left.\begin{matrix}Fe_2\\Fe\end{matrix}\right\}Cfy_2$, which, as we have seen, forms the chief constituent of prussian blue, and it appears highly probable that the two compounds are identical. Its formation is easily explained. By bringing together ferricyanide of potassium and a ferrous salt, a part of the latter is oxidized, a ferric salt being formed and a ferrocyanide, from which the mixture of the two iron salts then precipitates prussian blue:—

$$2K_3(CN)_6Fe + 3FeCl_2 + H_2O = 2HK_3(CN)_6Fe + FeO + Fe_2Cl_6 = \left.\begin{matrix}Fe_2\\ Fe\end{matrix}\right\}(Fe(CN)_6)_2 + H_2O + 6KCl$$

Hydric Ferricyanide, Hydroferricyanic Acid, H_3Cfdy.—To prepare this acid a solution of red prussiate of potash is precipitated with acetate of lead, and the precipitate, after washing, decomposed by dilute sulphuric acid. On evaporating the filtrate, the acid crystallizes in brown needles, which have a sour and astringent taste. Exposed to the air they give off prussic acid, and assume a blue colour.

NITROPRUSSIDES.

By adding a solution of potassium nitrite to the precipitate, produced by adding potassium cyanide to a solution of ferrous sulphate, *potassium nitroprusside* is formed, according to the following equation:—

$$KFe_2Cy_5 + KNO_2 = K_2FeCy_5NO + FeO.$$

An excess of the nitrite at the same time oxidizes the ferrous oxide to ferric oxide. The nitroprussides are distinguished by their fine red colour; the sodium salt, which crystallizes the best of all, is generally prepared from potassium ferrocyanide, by heating it with dilute nitric acid, until the solution no longer gives with ferrous sulphate a blue but a slate-coloured precipitate. During this reaction gases are evolved, containing nitrogen, carbon dioxide, cyanogen, and hydrocyanic acid. On cooling the solution, potassium nitrate crystallizes out, the mother liquor is neutralized with sodium carbonate, the solution concentrated by evaporation, and the nitroprusside separated from potassium and sodium nitrate by crystallization.

Sodium Nitroprusside Na_2FeCy_5NO forms ruby-red crystals. Its aqueous solution gives with alkaline sulphides an intense purple coloration, which soon disappears; it is therefore used as a reagent for the detection of soluble sulphides; free hydrogen sulphide is not coloured by it.

PLATINOCYANIDES.

By suspending a mixture of barium carbonate and platinum dichloride in boiling water, and passing hydrocyanic acid through the liquid, *barium platinocyanide* is formed, which, on cooling, crystallizes in large monoclinic prisms, $Pt(CN)_4Ba + 4H_2O$. This salt, like all other soluble platinocyanides, is remarkable for the beautiful colours which it exhibits, the crystals appearing green when viewed along the principal axis, sulphur-yellow at right angles to it, and in reflected light the faces of the crystals exhibit a blue violet lustre. By decomposing this salt with the sulphates of the other metals the whole series of platinocyanides can be obtained, amongst which the *magnesium salt* $Pt(CN)_4 Mg + 7H_2O$ is one of the most beautiful; it forms fine large square prisms, of a deep red colour by transmitted light; but when viewed by reflected light the sides of the prisms exhibit a brilliant beetle-green, and their extremities a deep blue or purple colour. On adding sulphuric acid to a solution of the platinum salt, *hydrogen platinocyanide* $Pt(CN)_4H_2$ is obtained, which crystallizes from a concentrated solution in long prisms, having a splendid vermilion colour, accompanied by a blue iridescence.

COMPOUNDS OF CYANOGEN WITH THE HALOID ELEMENTS.

Cyanogen Chloride CNCl.—To prepare this compound chlorine is passed in the absence of light into a mixture of one part of anhydrous hydrocyanic acid, and five parts of water, the vessel being surrounded by a freezing mixture. Cyanogen chloride separates out as a mobile colourless liquid, heavier than water. It possesses a very irritating odour, attacking the eyes and producing a copious flow of tears; it boils at 15·5°, and solidifies at −5°. The pure compound may be kept for years without undergoing any change, but in the impure state it very soon changes into the polymeric *cyanuric chloride*.

Cyanogen Bromide CNBr is a very volatile solid body, subliming in needles, soon changing however into cubes; it smells like the chloride.

Cyanogen Iodide CNI is easily obtained by heating an intimate mixture of mercuric cyanide and iodine. It forms fine colourless needles, and has a pungent smell. It is frequently found in large quantities in commercial iodine.

Cyanuric Chloride $(C_3N_3)Cl_3$.—This compound is formed as already mentioned by the polymerisation of cyanogen chloride, and is also obtained by acting in sunlight with chlorine on anhydrous hydrocyanic acid or its solution in ether. It crystallizes in shining needles or scales, which melt at 145° and boil at 190°. Its odour is, especially on heating, pungent and producing a flow of tears.

CYANIC ACID AND CYANATES.

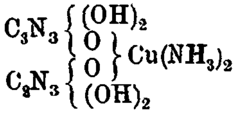
Metallic cyanides readily absorb oxygen, cyanates being formed. To prepare *potassium cyanate* KOCN, prussiate of potash and potassium carbonate are fused together, and red lead is gradually added. The melt is exhausted with hot spirits of wine; from this solution the salt crystallizes on cooling, in needles or plates. It is readily soluble in water; this solution soon undergoes decomposition, ammonia and acid potassium carbonate being formed:—

$$KOCN + 2H_2O = KHCO_3 + NH_3$$

Cyanic Acid $\left.\begin{matrix}CN\\H\end{matrix}\right\}O$.—Cyanates are readily decomposed by dilute acids, but the cyanic acid at the same time takes up water, and carbon dioxide and ammonia are formed. Therefore on adding a dilute acid to potassium cyanate effervescence takes place, carbon dioxide being given off, which has a pungent smell, due to the presence of a trace of cyanic acid. By acting on a cyanate with dry hydrochloric acid, cyanic acid is set free, which, however, at once combines with hydrochloric acid to form the compound $HCl.HOCN$, a colourless liquid, fuming in the air. From this compound also it is impossible to isolate cyanic acid because it at once changes into polymeric cyanuric acid $(CN)_3(OH)_3$. There is only one reaction by which cyanic acid can be obtained, and this is by the decomposition of cyanuric by heat, when it splits up into 3 mol. of cyanic acid, the vapours of which must be condensed by means of a freezing mixture. Cyanic acid is a colourless mobile liquid with a most pungent smell. On taking the vessel containing it out of the freezing mixture the liquid soon becomes turbid and hot, and with a crackling noise, or in large quantities with explosive ebullitions, is soon converted into a white porcelain-like mass, a polymeric modification, called *cyamelide*, the molecular weight of which is unknown. On heating cyamelide it is reconverted into cyanic acid.

Of the cyanates the most interesting salt is the *ammonium cyanate* $\left.\begin{matrix}CN\\NH_4\end{matrix}\right\}O$, obtained as a white crystalline mass, by mixing the vapour of dry cyanic acid with dry ammonia. The freshly prepared aqueous solution gives the reactions of cyanic acid and ammonia, but on standing for some time, or on heating, the ammonium cyanate is transformed into the isomeric *carbamide* or *urea*, $CO(NH_2)_2$. The dry salt also undergoes the same transformation on heating.

Cyanuric Acid $(CN)_3(OH)_3$.—On heating carbamide it behaves like the ammonium salt of this acid, splitting up into ammonia and cyanuric acid. The best method for preparing this compound is to pass dry chlorine over fused carbamide; nitrogen, hydrochloric acid, and vapours of sal-ammoniac are given off, and a residue is left, which is exhausted with cold water to remove ammonium chloride, and the remaining cyanuric acid is crystallized from boiling water. Cyanuric acid is also formed by boiling cyanuric chloride with a solution of caustic potash. It crystallizes in clear monoclinic prisms $(CN)_3(OH)_3 + 2H_2O$. When exposed to the air it loses water, and crumbles into a white powder. It is a tribasic acid; of its salts the sodium salt is most characteristic, from the fact that it is only sparingly soluble in a hot concentrated solution of caustic soda, and therefore separates in fine needles on heating a cold saturated solution. By adding an ammoniacal solution of copper sulphate to an aqueous solution of cyanuric acid, a crystalline violet precipitate is formed, having the formula:—

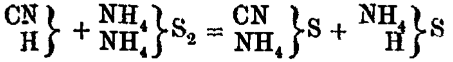


$$\left.\begin{array}{l}C_3N_3\left\{\begin{array}{l}(OH)_2\\ O\end{array}\right.\\ C_3N_3\left\{\begin{array}{l}O\\ (OH)_2\end{array}\right.\end{array}\right\}Cu(NH_3)_2$$

SULPHOCYANIC ACID AND SULPHOCYANATES.

Potassium Sulphocyanate $\left.\begin{array}{l}CN\\ K\end{array}\right\}S$.—To prepare this salt, anhydrous potassium ferrocyanide, potassium carbonate, and sulphur are fused together, and the melt exhausted with spirits of wine. On evaporating this solution the salt crystallizes in large colourless prisms. It is very readily soluble in water, the temperature being at the same time so much lowered that it is sometimes used as a freezing mixture. On mixing 500 grams with 400 grams of cold water the temperature goes down to − 20°.

Ammonium Sulphocyanate $\left.\begin{array}{l}CN\\ NH_4\end{array}\right\}S$, is formed by heating prussic acid with yellow ammonium sulphide:—



$$\left.\begin{array}{r}CN\\ H\end{array}\right\} + \left.\begin{array}{l}NH_4\\ NH_4\end{array}\right\}S_2 = \left.\begin{array}{l}CN\\ NH_4\end{array}\right\}S + \left.\begin{array}{r}NH_4\\ H\end{array}\right\}S$$

The best method to prepare it in quantity is to mix carbon disulphide with alcohol and strong aqueous ammonium, and distil the alcohol off after some time. On evaporating the residue on a water bath the ammonium sulphocyanate crystallizes out. The reaction which takes place will be explained under sulphocarbonic acid. Ammonium sulphocyanate crystallizes in colourless deliquescent plates, which melt at 147°, and readily dissolve in water, with the production of cold. When heated for some time to 170° it is transformed into the isomeric sulphocarbamide.

Sulphocyanates of Mercury.—The two nitrates of mercury are precipitated by soluble sulphocyanates. The mercuric sulphocyanate is decomposed by heat, the mass swelling up and leaving a very voluminous residue behind. It is used for the preparation of the so-called Pharaoh's Serpents.

Sulphocyanic Acid $\left.\begin{array}{l}CN\\ H\end{array}\right\}S$.—To obtain the anhydrous acid, sulphuretted hydrogen is passed over heated mercuric sulphocyanate. It is a colourless, oily liquid, having a pungent odour, like acetic acid, and solidifying at $-12{\cdot}5°$. It readily undergoes decomposition, prussic acid being given off, and a yellow crystalline residue left behind, which has been called *persulphocyanic acid* $H_2C_2N_2S_3$. Aqueous sulphocyanic acid can be obtained by distilling potassium sulphocyanate with dilute sulphuric acid, but a part of the acid easily undergoes a change by taking water up and forming ammonia and carbon oxysulphide COS, a decomposition analogous to the formation of ammonia and carbon dioxide from cyanic acid. By adding ferric chloride to a solution of sulphocyanic acid or a sulphocyanate the liquid assumes a deep blood-red colour. This very characteristic reaction is caused by the formation of *ferric sulphocyanide* $\left.\begin{matrix}(CN)_6\\ Fe_2\end{matrix}\right\} S_6$, a salt which may be obtained in small blackish red crystals on evaporating a solution of ferric hydroxide in sulphocyanic acid.

Cyanogen Sulphide $\left.\begin{matrix}CN\\ CN\end{matrix}\right\} S$, is formed by heating a mixture of cyanogen iodide and silver sulphocyanate :—

$$\left.\begin{matrix}CN\\ I\end{matrix}\right\} + \left.\begin{matrix}CN\\ Ag\end{matrix}\right\} S = \left.\begin{matrix}I\\ Ag\end{matrix}\right\} + \left.\begin{matrix}CN\\ CN\end{matrix}\right\} S.$$

It sublimes in transparent rhombic plates, which smell like cyanogen iodide, and readily dissolve in water, alcohol, and ether. By caustic potash it is decomposed thus :—

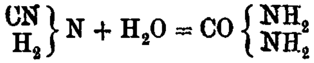
$$\left.\begin{matrix}CN\\ CN\end{matrix}\right\} S + 2\left.\begin{matrix}K\\ H\end{matrix}\right\} O = \left.\begin{matrix}CN\\ K\end{matrix}\right\} S + \left.\begin{matrix}CN\\ K\end{matrix}\right\} O + \left.\begin{matrix}H\\ H\end{matrix}\right\} O.$$

Isosulphocyanates.—When persulphocyanic acid is treated with an alcoholic solution of potash, it yields *potassium isosulphocyanate*, which is obtained by slow evaporation from an aqueous solution in hard crystals having the composition $CSNK + H_2O$. This body may be easily distinguished from potassium sulphocyanate by adding to its aqueous solution a drop of ferric chloride, a brown coloration being produced, which disappears again on adding more of the ferric salts. When the isosulphocyanate is heated, it melts and undergoes a molecular change, being transformed into the common sulphocyanate.

The free isosulphocyanic acid has not yet been obtained, but we are acquainted with a series of ethers of this acid, of which the best known is oil of mustard or allyl isosulphocyanate, having the constitution $N\left\{\begin{matrix}CS\\ C_3H_5\end{matrix}\right.$, from which it follows that isosulphocyanic acid is *sulphocarbimide* $N\left\{\begin{matrix}CS\\ H\end{matrix}\right.$.

AMIDES OF CYANOGEN.

Cyanamide $\left.\begin{matrix}CN\\ H\\ H\end{matrix}\right\} N$.—On passing gaseous cyanic acid into a solution of ammonia in ether, ammonium chloride separates out, and the solution yields on evaporation cyanamide in colourless crystals, which melt at 40° and are readily soluble in water. On adding nitric acid to its aqueous solution it is converted into carbamide :—

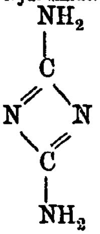


$$\left.\begin{matrix}CN\\H_2\end{matrix}\right\}N + H_2O = CO\left\{\begin{matrix}NH_2\\NH_2\end{matrix}\right.$$

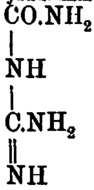
Dicyanamide or Parame $C_2N_2\left\{\begin{matrix}NH_2\\NH_2\end{matrix}\right.$.—This polymeric modification is formed on adding ammonia to an aqueous solution of cyanamide when, after some time, the parame crystallizes out in rhombic plates, which are readily soluble in water and alcohol, and sparingly in ether; it melts at 205°. By evaporating the aqueous solution, in presence of an acid, *dicyandiamine* $C_2H_6N_4O$ is formed, a white crystalline substance, which forms with water a strongly alkaline solution, and combines with acids forming crystalline salts.

The constitution of these compounds is probably the following:—

Dicyanamide.



Dicyandiamine.



Cyanuric Amide or Melamine $C_3N_3\left\{\begin{matrix}NH_2\\NH_2\\NH_2\end{matrix}\right.$.—On heating cyanamide to 150° a violent reaction sets in, melamine being formed, which crystallizes in shining, rhombic octahedrons, readily soluble in water but insoluble in alcohol and ether. It combines like ammonia with acids, forming compounds like $C_3H_3(NH_2)_3HCl$.

When cyanuric amide is boiled with dilute nitric acid it assimilates water, ammonia is formed, and it is converted successively into

Ammeline	$C_3H_5N_5O$
Ammelide . , . .	$C_3H_4N_4O_2$
Cyanuric Acid . . .	$C_3H_3N_3O_3$.

Ammeline $C_3N_3\left\{\begin{matrix}(NH_2)_2\\OH\end{matrix}\right.$ is a powder insoluble in water, alcohol, and ether, but soluble in alkalies and acids, and forms salts which are decomposed by water.

Ammelide $C_3N_3\left\{\begin{matrix}NH_2\\(OH)_2\end{matrix}\right.$ is a white powder which, like ammeline, dissolves in alkalis and acids, but does not combine with the latter. Its ammoniacal solution gives with silver nitrate a white precipitate having the composition $C_3N_3(NH_2)\left\{\begin{matrix}OH\\OAg.\end{matrix}\right.$

Phosphorus Tricyanide $P(CN)_3$.—To prepare this compound silver cyanide and phosphorus trichloride, diluted with chloroform, are heated in sealed tubes. After cooling, the contents of the tubes are heated in a retort, through which a current of carbon dioxide is passed; at 160° the phosphorus tricyanide begins to sublime in long white needles or plates. On gently heating them in the air they take fire, and by water they are resolved into prussic acid and phosphorous acid:—

$$P(CN)_3 + 3H_2O = 3CNH + PO_3H_3$$

CARBONYL AND SULPHOCARBONYL COMPOUNDS.

The dyad radical carbonyl CO exists in the free state as carbon monoxide; it is a non-saturated compound combining directly with several elements or radicals, forming the following compounds:—

$CO.O$	Carbonyl Oxide or Carbon Dioxide.	$CO\left\{\begin{matrix}OK\\OH\end{matrix}\right.$	Hydric Potassium Carbonate.
$CO\left\{\begin{matrix}OK\\OK\end{matrix}\right.$	Potassium Carbonate.	$CO.S$	Carbonyl Sulphide.
$CO\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.$	Carbonyl Chloride	$CO\left\{\begin{matrix}NH_2\\NH_2\end{matrix}\right.$	Carbamide.

The sulphocarbonyl compounds contain the dyad radical sulphocarbonyl CS, which is not known in the free state, but from which the following compounds are derived:—

$CS.S$ Sulphocarbonyl sulphide or carbon disulphide.

$CS\left\{\begin{matrix}SH\\SH\end{matrix}\right.$	Sulphocarbonic Acid.	$CS\left\{\begin{matrix}SK\\SK\end{matrix}\right.$	Potassium Sulphocarbonate.
$CS\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.$	Sulphocarbonyl Chloride.	$CS\left\{\begin{matrix}NH_2\\NH_2\end{matrix}\right.$	Sulphocarbamide.

Carbon Monoxide or Carbonyl CO.—This gas is always formed by the abstraction of oxygen from carbon dioxide or carbonates; thus it is obtained by passing carbon dioxide over red-hot charcoal, or by heating chalk with iron or zinc:—

$$\begin{aligned} CO_2 + C &= 2CO \\ CaCO_3 + Zn &= CaO + ZnO + CO \end{aligned}$$

It is also produced by heating certain metallic oxides, such as those of iron, zinc, lead, &c., with charcoal, and further occurs as a product of the decomposition of several carbon compounds; for instance, formic acid when heated with strong sulphuric acid is resolved into water and carbon monoxide:—

$$\left.\begin{matrix}COH\\H\end{matrix}\right\}O = CO + \left.\begin{matrix}H\\H\end{matrix}\right\}O$$

By acting with sulphuric acid on oxalic acid, water is formed, and a mixture of equal volumes of carbon monoxide and dioxide is given off:—

$$\left.\begin{matrix}CO.OH\\CO.OH\end{matrix}\right\} = CO + CO_2 + H_2O$$

The most convenient method for preparing carbon monoxide is to heat coarsely powdered potassium ferrocyanide with eight times its weight of commercial sulphuric acid; this acid contains about 10—15 per cent. of water, which take part in the reaction. In the first stage prussic acid is set free, which by the action of the sulphuric acid is transformed into ammonia and formic acid, and the latter then splits up into water and carbon monoxide. The final reaction is expressed by the following equation:—

$$K_4FC_6N_6 + 6H_2SO_4 + 6H_2O = 6CO + K_2SO_4 + 3(NH_4)SO_4 + FeSO_4$$

Carbon monoxide is a colourless, tasteless gas, which has not yet been condensed to a liquid; its specific gravity is 0·969. It is but sparingly soluble in water, and acts as a strong poison, producing death when inhaled even in small quantities. It is readily inflammable, burning with a characteristic blue flame, and it acts as a reducing agent on many metallic oxides, which when heated in this gas part with their oxygen:—

$$Fe_2O_3 + 3CO = 2Fe + 3CO_2$$

Chlorine and carbon monoxide combine under the influence of sunlight, carbonyl chloride $COCl_2$ being formed, and by heating carbon monoxide with caustic potash it is absorbed with the formation of potassium formate:—

$$CO + \left.\begin{matrix}H\\K\end{matrix}\right\}O = \left.\begin{matrix}COH\\K\end{matrix}\right\}O$$

It also combines with metallic potassium; from the compound $C_2O_2K_2$ thus produced a series of remarkable acids is derived, which will be described later on.

Carbon Dioxide CO_2 is always produced by heating carbon or carbon compounds with an excess of oxygen, and is also formed by different processes of slow oxidation, as in those of respiration, putrefaction, &c. It exists in the free state in the air and in mineral springs, and is emitted in large quantities from the craters of active volcanoes as well as from fissures in districts of extinct volcanic action.

To prepare pure carbon dioxide a carbonate is decomposed by an acid; calcium carbonate (chalk or marble) and hydrochloric acid, or sodium bicarbonate and dilute sulphuric acid being usually employed.

Carbon dioxide is a colourless, inodorous gas, possessing a pungent, slightly acid taste. It is tolerably soluble in water, more readily in cold than in warm, and is found in all spring water, which owes its refreshing taste to the presence of this gas; it is contained in larger quantities in soda-water, champagne, and other sparkling drinks, which have been saturated with this gas under pressure.

By the application of strong pressure or by exposure to a very low temperature it is condensed to a mobile liquid, boiling at $-78°$, which on rapid evaporation absorbs so much heat that a part of it freezes to a snow-like mass. When a tube containing liquid carbon dioxide is placed in liquid ammonia allowed to evaporate very quickly, so much cold is produced that the carbon dioxide solidifies to a transparent ice-like mass, which by pressure is easily divided into cubical crystals. On heating potassium or magnesium in carbon dioxide a carbonate is formed with the separation of finely divided carbon.

Carbonic Acid and Carbonates.—The aqueous solution of carbon dioxide has a slight *acid* reaction, and may be considered to contain the dibasic carbonic acid. This latter body, however, has not yet been isolated, but from it is derived a series of salts, called carbonates:—

$$\mathrm{CO}\left\{\begin{matrix}\mathrm{OH}\\\mathrm{OH}\end{matrix}\right. \text{ Carbonic Acid.} \qquad \mathrm{CO}\left\{\begin{matrix}\mathrm{OK}\\\mathrm{OH}\end{matrix}\right. \begin{matrix}\text{Hydric Potassium}\\\text{Carbonate.}\end{matrix}$$

$$\mathrm{CO}\left\{\begin{matrix}\mathrm{OK}\\\mathrm{OK}\end{matrix}\right. \begin{matrix}\text{Normal Potassium}\\\text{Carbonate.}\end{matrix} \qquad \mathrm{CO}\left\{\begin{matrix}\mathrm{O}\\\mathrm{O}\end{matrix}\right\}\mathrm{Ca} \text{ Calcium Carbonate.}$$

The carbonates of the alkaline metals are soluble in water, those of the other metals insoluble. By passing carbon dioxide into lime-water or baryta-water a white precipitate is formed, a most characteristic reaction of carbon dioxide.

When moist carbon dioxide is brought in contact with potassium formic acid is produced:—

$$2\mathrm{CO}_2 + \mathrm{O}\left\{\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right. + \mathrm{K}_2 = \mathrm{CO}\left\{\begin{matrix}\mathrm{OH}\\\mathrm{OK}\end{matrix}\right. + \mathrm{CO}\left\{\begin{matrix}\mathrm{H}\\\mathrm{OK}\end{matrix}\right.$$

When carbon dioxide is passed over strongly heated sodium it combines with it and forms sodium oxalate:—

$$\begin{matrix}\mathrm{CO}_2 & & \mathrm{Na} & & \mathrm{CO.ONa}\\ & + & & = & |\\ \mathrm{CO}_2 & & \mathrm{Na} & & \mathrm{CO.ONa}\end{matrix}$$

Carbonyl Chloride COCl_2.—This compound, also called *carbon oxychloride* or *phosgene gas*, is obtained by exposing a mixture of equal volumes of pure carbon monoxide and dry chlorine in large white glass balloons to the sunlight (φῶς and γενάω). In preparing it a slight excess of chlorine is used, and the gas after combination has taken place is passed through a tube filled with metallic antimony, by which the free chlorine is absorbed. Carbonyl chloride is a colourless gas, fuming strongly in the air, and possessing a most unpleasant suffocating odour. By the application of cold it is condensed to a mobile liquid boiling at $+8°$; it is heavier than water, which, however, rapidly acts on it, carbon dioxide and hydrochloric acid being formed :—

$$COCl_2 + H_2O = CO_2 + 2HCl$$

Carbonyl chloride is also formed by heating chloroform with potassium dichromate and an excess of sulphuric acid :—

$$2CHCl_3 + 2CrO_3 = 2COCl_2 + Cl_2 + H_2O + Cr_2O_3$$

By exposing a mixture of bromine vapour and carbon monoxide, to the sunlight carbonyl dibromide $COBr_2$ is formed, a compound which is very little known.

Carbamic Acid $CO\left\{\begin{matrix}NH_2\\OH\end{matrix}\right.$ is not known in the free state; its ammonium salt $CO\left\{\begin{matrix}NH_2\\ONH_4\end{matrix}\right.$ is obtained by mixing dry carbon dioxide with dry ammonia. It is a white solid, which is very volatile, being decomposed at a gentle heat into its constituents. It dissolves in water, forming ammonium carbonate. Other metallic carbamates have not yet been obtained, but there exists a series of ethers of this acid or compounds containing alcohol radicals in the place of the hydrogen of the hydroxyl.

Carbamide or Urea $CO\left\{\begin{matrix}NH_2\\NH_2\end{matrix}\right.$.—This body is formed when carbonyl chloride is acted upon by dry ammonia :—

$$CO\left\{\begin{matrix}Cl\\Cl\end{matrix}\right. + 4NH_3 = CO\left\{\begin{matrix}NH_2\\NH_2\end{matrix}\right. + 2NH_4Cl$$

It is also produced when ammonium carbonate or the commercial sesquicarbonate are heated to 130° to 140° in closed tubes :—

$$CO\left\{\begin{matrix}NH_2\\ONH_4\end{matrix}\right. = CO\left\{\begin{matrix}NH_2\\NH_2\end{matrix}\right. + H_2O$$

Carbamide occurs in the urine of mammals, birds, and reptiles, and is also found in other animal liquids; it was known for a long time before its constitution was determined, by the name of *urea*. It may be obtained from urine by evaporating it to the consistency of a syrup, and adding to the cold residue strong, pure nitric acid, which precipitates urea nitrate, a salt easily purified by recrystallization. Urea is, however, most conveniently prepared from ammonium cyanate, a compound which, as has already been mentioned, undergoes on heating a remarkable molecular change, being transformed into urea.

To obtain it by this method eight parts of anhydrous potassium ferrocyanide are fused with three parts of potassium carbonate, and fifteen parts of red lead are gradually added. The cooled mass is exhausted with water, and the solution of potassium cyanate is evaporated with eight parts of ammonium sulphate. The dry residue, consisting of potassium sulphate and urea, is treated with warm alcohol, by which the latter compound is dissolved.

Urea can be reconverted into a cyanate; thus on evaporating its aqueous solution with silver nitrate, ammonium nitrate and silver cyanate are formed.

Urea crystallizes in colourless needles or long striated prisms; it is readily soluble in water and alcohol, but almost insoluble in ether, and has a cooling taste like saltpetre. Its solution has a neutral reaction, yet urea has marked basic properties, combining like ammonia with acids, forming crystalline salts.

Urea Nitrate $CO(NH_2)_2.NO_3H$ is readily soluble in water, but only sparingly in strong nitric acid, and is therefore obtained as a crystalline precipitate by adding nitric acid to an aqueous solution of urea; from water it crystallizes in long prisms.

Urea Oxalate $2[CO(NH_2)_2].C_2O_4H_2$ is obtained as a white crystalline precipitate by mixing solutions of oxalic acid and urea; it is only sparingly soluble in water.

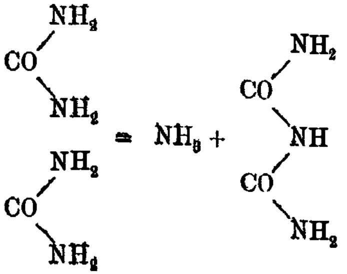
Urea also enters into combination with metallic oxides and several salts. Mercuric nitrate produces in a solution of urea a white precipitate having the composition $2CO(NH_2)_2 + 3HgO + Hg(NO_3)_2$. This reaction is made use of to determine the quantity of urea in urine. Two volumes of urine are mixed with one volume of a mixture consisting of equal volumes of baryta-water and a cold saturated solution of barium nitrate, in order to precipitate the phosphates and sulphates contained in urine. To 15 cb.cm. of the filtrate (corresponding to 10 cb.cm. of urine) a solution of mercuric nitrate of known *titre* is added by means of a burette, as long as a precipitate is formed. The end of the reaction is easily recognized by adding a solution of sodium carbonate to a drop of the liquid, which assumes a yellow coloration as soon as a slight excess of mercury has been added. It is convenient to have the mercury solution of such a strength, that 1 cb.cm. should correspond to 0·01 gram of urea.

When urea and water are heated together in sealed tubes to above 100°, carbonic dioxide and ammonia are produced; the same change occurs in the putrefaction of urine. This reaction may also be used for the quantitative determination of urea; the urine has only to be heated with an ammoniacal solution of barium chloride, and the barium carbonate formed, to be weighed.

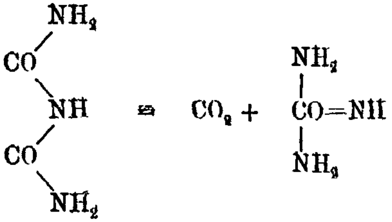
Nitrogen trioxide acts readily upon urea, as it does on all other amido-compounds, the products of the reaction being carbon dioxide, water, and free nitrogen:—

$$CO\left\{\begin{matrix}NH_2\\NH_2\end{matrix}\right. + N_2O_3 = 2N_2 + CO_2 + 2H_2O$$

Biuret $C_2H_5N_3O_2$ is formed when urea is heated to 150°—160°:—



Biuret is sparingly soluble in cold, but more readily in hot water, from which it crystallizes in colourless needles. On heating it above 170°, ammonia escapes and cyanuric acid is left behind, and when it is heated in a current of dry hydrochloric acid, carbon dioxide and *guanidine* CH_5N_3 are formed, together with cyanuric acid:—



Guanidine is a strong base, which will be described later on.

Isuretine CH_4N_2O.—This isomeride of urea is produced by digesting an alcoholic solution of hydroxylamine with strong hydrocyanic acid at 40°—50°. By evaporation it is obtained in long, colourless crystals, having a strong alkaline reaction and melting at 104°. The hydrochloride $CH_4N_2O.HCl$ forms deliquescent rhombic plates; the sulphate and oxalate are also crystallizable.

Heated above its melting-point isuretine readily decomposes, giving a considerable sublimate of ammonium carbonate and yielding a residue containing *ammelide* (p. 61).

An aqueous solution of isuretine evaporated on a water bath undergoes decomposition with evolution of nitrogen, ammonia, and carbon dioxide, and a residue is left containing *urea* and *biuret*. The constitution of isuretine is probably expressed by one of the following formulæ:—

$$C\left\{\begin{array}{l}NH\\ NH.OH\\ H\end{array}\right. \text{ or } C\left\{\begin{array}{l}NH\\ O.NH_2\\ H\end{array}\right.$$

Hydroxyl Carbamide $CO\left\{\begin{array}{l}NH(OH)\\ NH(OH)\end{array}\right.$ is produced by acting upon cyanic acid with hydroxylamine $NH_2(OH)$. To prepare it a solution of hydroxylammonium nitrate is cooled down to − 10°, and mixed with a concentrated aqueous solution of potassium cyanate. It crystallizes in white needles, melting at 130°.

Carbonyl Sulphide or Carbon Oxysulphide COS.—This compound is formed by passing carbon monoxide and sulphur vapour through a red-hot porcelain tube. It is, however, best prepared by adding potassium sulphocyanate to a cold mixture of four parts of water and five parts of concentrated sulphuric acid, the sulphocyanic acid which is first set free, taking up water, forms ammonia and carbonyl sulphide:—

$$\left.\begin{matrix}CN\\H\end{matrix}\right\}S + H_2O = COS + NH_3$$

Carbonyl sulphide is a colourless gas possessing a peculiar resinous smell, resembling at the same time that of hydrogen sulphide; it is very inflammable, burning with a blue flame. It is slightly soluble in water, and appears to occur in some sulphur springs. Caustic potash absorbs it but slowly, potassium carbonate and sulphide being formed:—

$$COS + 4\ KOH = K_2CO_3 + K_2S + 2H_2O$$

Carbon Disulphide CS_2 is obtained as a heavy colourless liquid by passing sulphur vapour over red-hot charcoal. The commercial product has a very unpleasant odour, due to impurities contained in it; these may be destroyed by heating the crude sulphide with water in closed tubes to 100°.

Pure carbon disulphide boils at 43·3°, and possesses an ethereal odour. On evaporating it rapidly, by means of a strong current of air, so much heat becomes latent that a portion of the sulphide solidifies to a white mass resembling cauliflowers, and melting again at − 12°. Carbon disulphide is insoluble in water, and has at 0° the specific gravity 1·0272; it is highly inflammable: its vapour, when mixed with air, takes fire at 149°. It is poisonous; the inhalation of its vapour produces giddiness, congestion, and vomiting. It is manufactured on a large scale, as it is found to be an excellent solvent for resins, oils, fats, caoutchouc, phosphorus, sulphur, &c. On account of its inflammability and poisonous properties great care must be taken in using it.

Sulphocarbonic Acid and Sulphocarbonates.—Just as carbon dioxide and metallic oxides combine to form carbonates, carbon disulphide combines with metallic sulphides, forming *sulphocarbonates.* Sodium sulphocarbonate CS_3Na_2 is obtained by dissolving carbon disulphide in a solution of sodium sulphide; on adding alcohol to this solution the compound separates out as a thick brownish red liquid, from which the free sulphocarbonic acid may be obtained by adding hydrochloric acid and water; it is a heavy brown oil having a peculiar disagreeable odour. The sulphocarbonates of the metals of the alkalis and alkaline earths are soluble in water; those of the other metals are insoluble.

Sulphocarbonyl Chloride $CSCl_2$ is a colourless liquid possessing an irritating smell; it boils at 70° and is formed amongst other products by the action of chlorine upon carbon disulphide.

Sulphocarbamic Acid $CS\left\{\begin{matrix}NH_2\\SH\end{matrix}\right.$.—The ammonium salt of this acid is formed together with ammonium sulphocarbonate by adding carbon disulphide to a solution of ammonia in absolute alcohol. It crystallizes in large yellow prisms; on heating it to 100° it is decomposed, with the formation of ammonium sulphocyanate and hydrogen sulphide:—

$$CS\left\{\begin{matrix}NH_2\\SNH_4\end{matrix}\right. = \left.\begin{matrix}CN\\NH_4\end{matrix}\right\}S + SH_2$$

The free sulphocarbamic acid is obtained by decomposing the ammonium salt with hydrochloric acid; it is a reddish oil, which soon decomposes into hydrogen sulphide and sulphocyanic acid.

Sulphocarbamide or Sulphur Urea $CS\left\{\begin{matrix}NH_2\\NH_2\end{matrix}\right.$ is formed by heating ammonium sulphocyanate for some hours to 170°; a molecular change takes place analogous to the transformation of ammonium cyanate into urea. Sulphocarbamide crystallizes in silky needles and combines like common urea with acids; the nitrate crystallizes exceedingly well. When sulphocarbamide is heated above 170°, carbon disulphide, hydrogen sulphide, and ammonia are given off, and a yellowish powder called *mellam* $C_{11}H_9N_{11}$ is left behind.

ACIDS FROM POTASSIUM CARBOXIDE.

On passing carbon monoxide over fused potassium the gas is absorbed, the metal being converted into a black porous mass, having the composition $C_2O_2K_2$; the same body is formed as a byeproduct in the manufacture of potassium. It is not altered in dry air, but in presence of moisture it soon colours red and afterwards yellow. By water it is decomposed with great violence, and often with an explosion. By adding the freshly prepared compound very cautiously to dilute hydrochloric acid, *trihydrocarboxylic acid* $C_2O_2H_2$ is formed, crystallizing in white needles. Its colourless solution darkens when it is exposed to the air, and black needles of *bihydroxylic acid* $C_3H_3H_2$ gradually crystallize out, whilst the compound $C_2O_2K_2$, after having been exposed a short time to moist air, yields *hydrocarboxylic acid* $C_4O_4H_2$. When the black mass has become red by longer exposure to the air, it contains the potassium salt of *rhodizonic acid* $C_5O_6H_4$; the free acid is obtained by acting on the red mass with hydrochloric acid. It forms colourless needles, which lose water at 100° and turn black. Rhodizonic acid is bibasic; the silver salt $C_5O_6H_2Ag_2$ is a red precipitate. On boiling a solution of potassium rhodizonate with potash, *potassium croconate* $C_5O_5K_2$ is formed, a salt which is also contained in the original substance after being coloured yellow by long exposure to the air. Free croconic acid $C_5H_5H_2$ is obtained by adding sulphuric acid and alcohol to the potassium salt and evaporating the solution; it crystallizes in yellow laminæ. Both rhodizonic and croconic acid are oxidized by nitric acid to *leuconic acid* $C_5O_9H_8$, which is tribasic and obtained as a colourless syrup by adding alcohol to the aqueous solution.

Neither the molecular weights nor the constitution of these remarkable compounds are known.

HYDROCARBONS OF THE SERIES $C_{2n}H_{n+2}$ OR PARAFFINS.

Of the hydrocarbons homologous with marsh-gas those containing less than five atoms of carbon are gases at the ordinary temperature; the next higher ones are mobile, colourless liquids, having a faint but characteristic ethereal odour; and those richest in carbon are crystalline solids. A mixture of the latter has been known for a long time under the name of paraffin (*parum affinis*), a name given to them from the fact that they resist in the cold the action of strong oxidizing agents. But as the gaseous and liquid hydrocarbons of this group show the same resistance against nitric acid, chromic acid, &c., it appears appropriate to give to the whole group the name the *paraffins*. Whilst they are not acted upon in the cold even by a mixture of fuming nitric and sulphuric acids, on the application of heat they are oxidized, even by dilute nitric acid, the products consisting of carbon dioxide and water, besides small quantities of fatty acids, succinic acid, and nitriles, whilst chromic acid produces carbon dioxide and water, as well as a little acetic acid.

By acting on the paraffins with chlorine in diffused daylight, substitution products are formed, the first product being the chloride of a monad radical, marsh-gas or methane yielding methyl chloride:—

$$CH_4 + Cl_2 = CH_3Cl + HCl$$

By continued action of chlorine a further exchange of chlorine for hydrogen takes place; thus from marsh-gas the following bodies have been obtained:—

$$\begin{aligned} CH_4 &+ Cl_2 = CH_3Cl &+ HCl \\ CH_3Cl &+ Cl_2 = CH_2Cl_2 &+ HCl \\ CH_2Cl_2 &+ Cl_2 = CHCl_3 &+ HCl \\ CHCl_3 &+ Cl_2 = CCl_4 &+ HCl \end{aligned}$$

In the same way the six atoms of hydrogen in ethane C_2H_6 have been substituted one after the other by chlorine, whilst in propane C_3H_8 and hexane C_6H_{14} only six have thus been replaced.

When chlorine is passed into a liquid paraffin, a portion of the monochloride first formed is always further acted upon by chlorine before all the hydrocarbon has been attacked, but the formation of such higher chlorides can be almost completely avoided, when chlorine is brought in contact with the vapour of the boiling hydrocarbon; the monochlorides being less volatile condense at once, and thus are brought out of the reach of an excess of chlorine.

Bromine acts on the paraffins in a manner similar to that of chlorine, only much less energetically, whilst iodine has no action whatever.

The monochlorides can by double decompositions easily be transformed into the alcohols and other derivatives. Thus on heating methyl chloride with caustic potash we obtain methyl alcohol:—

$$CH_3Cl + KOH = ClK + CH_3.OH$$

By heating the chlorides with concentrated hydriodic acid, the iodides are formed; which compounds are also obtained by acting upon alcohols with hydriodic acid. Thus amyl alcohol yields amyl iodide:—

$$C_5H_{11}.OH + HI = C_5H_{11}I + H_2O$$

On the other hand these derivatives of the paraffins can again be transformed into the original hydrocarbons. Thus by treating the substitution products of marsh-gas with zinc and hydrochloric acid, an *inverse substitution* takes place, hydrogen again replacing one atom of chlorine after the other:—

$$\begin{aligned} CCl_4 + H_2 &= CH\,Cl_3 + HCl \\ CH\,Cl_3 + H_2 &= CH_2Cl_2 + HCl \\ CH_2Cl_2 + H_2 &= CH_3Cl + HCl \\ CH_3Cl + H_2 &= CH_4 + HCl \end{aligned}$$

The iodides are even more easily reduced by the same reaction, and thus from any alcohol the corresponding paraffin may be obtained. The alcohols of dyad, triad, tetrad, and hexad radicals can also be converted into paraffins, inasmuch as these bodies are readily transformed into iodides of monad radicals by the action of hydriodic acid. Thus mannite $C_6H_8(OH)_6$ yields hexyl iodide:—

$$C_6H_8(OH)_6 + 11HI = C_6H_{13}I + 6H_2O + 5I_2$$

And this iodide is transformed by nascent hydrogen into hexane:—

$$C_6H_{13}I + H_2 = C_6H_{14} + HI$$

Instead of acting on the iodides with nascent hydrogen they may be heated with zinc and water in sealed tubes to 150°, when basic zinc iodide and a paraffin are formed:—

$$C_5H_{11}I + H_2O + Zn = C_5H_{12} + Zn\left\{\begin{matrix} I \\ OH \end{matrix}\right.$$

The paraffins obtained from the iodides by these two methods have been called *hydrides;* methane being considered as methyl hydride $\left.\begin{matrix}CH_3\\H\end{matrix}\right\}$ and hexane as *hexyl hydride* $\left.\begin{matrix}C_6H_{13}\\H\end{matrix}\right\}$. But from these names it might appear that the paraffins contain one atom of hydrogen combined with carbon in a manner different from that in which the remainder of the hydrogen is attached to the carbon, which is not the case; for on further action of chlorine on the monochlorides we obtain chlorides of dyad, triad, &c. radicals, propane for instance yielding :—

Propyl Chloride.	Propene Dichloride.	Propenyl Trichloride.
C_3H_7Cl	$C_3H_6Cl_2$	$C_3H_5Cl_3$

And therefore propane might be called propene hydride and propenyl hydride, as well as propyl hydride.

A second general method to obtain paraffins is to act with a metal upon an iodide of an alcohol radical; in this reaction the radicals are set free, but as a monad radical, as we have seen, cannot exist in the free state, two of them are linked together by the two free combining units. Thus by heating dry methyl iodide and zinc to 150°, ethane is formed :—

$$2CH_3 + Zn = C_2H_6 + ZnI_2$$

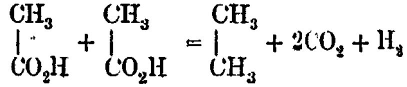
Sodium acts violently upon a mixture of ethyl and amyl iodide, the hydrocarbon C_7H_{16} being formed :—

$$C_2H_5I + C_5H_{11}I + Na_2 = C_7H_{16} + 2NaI$$

The paraffins formed by this synthetical process have been called *alcohol radicals,* because it was formerly believed that their constitution was different from the so-called hydrides; they were regarded as the free radicals, of which two were united to form a molecule, just as the molecule of hydrogen consists of two atoms. But we now know that *hydride of ethyl* is identical with *dimethyl;* both possessing the same physical and chemical properties, and yielding by the action of chlorine as the first product, ethyl chloride.

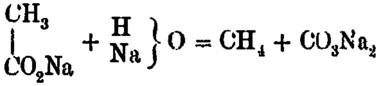
In *ethyl-amyl* one atom of carbon in the ethyl group is linked to one atom of carbon in amyl, exactly in the same manner as all the other carbon atoms are attached to each other, and thus on acting with chlorine on this hydrocarbon, we obtain *heptyl chloride* $C_7H_{15}Cl$, and not, as might have been expected according to the old theory, a mixture of ethyl chloride and amyl chloride.

A third general method of obtaining paraffins consists in the decomposition of an alkaline salt of a fatty acid by the galvanic current. When an acid or a salt is decomposed by electrolysis, the basic hydrogen or the metal is set free from the − pole, and the remainder of the compound from the + pole. The first action of a galvanic current upon a concentrated solution of potassium acetate is consequently to resolve the salt into K and $C_2H_3O_2$. But as this decomposition takes place in presence of water, the latter is acted upon by the potassium, and hydrogen is given off from the − pole, whilst the group $C_2H_3O_2$, which cannot exist in the free state, is decomposed into carbon dioxide and methyl CH_3, of which latter two combine to form ethane. This electrolysis of acetates may be expressed by the following equation :—



$$\begin{array}{l}CH_3\\ |\\ CO_2H\end{array} + \begin{array}{l}CH_3\\ |\\ CO_2H\end{array} = \begin{array}{l}CH_3\\ |\\ CH_3\end{array} + 2CO_2 + H_2$$

Paraffins are also formed by heating the fatty acids and the acids of the series $C_nH_{2n}(CO_2H)_2$ with an alkali. When sodium acetate is heated strongly with caustic soda, pure methane is given off :—



$$\begin{array}{l}CH_3\\ |\\ CO_2Na\end{array} + \left.\begin{array}{l}H\\ Na\end{array}\right\}O = CH_4 + CO_3Na_2$$

By heating suberic acid with caustic baryta hexane is formed :—

$$C_6H_{12}\left\{\begin{array}{l}CO_2H\\ CO_2H\end{array}\right. + 2BaO = C_6H_{14} + 2CO_3Ba$$

There is one method by which, it appears, paraffins can be obtained from almost every carbon compound. This method consists in heating the substance with a large excess of fuming hydriodic acid in sealed tubes to a very high temperature. The products consist of one or several paraffins, besides free iodine, oxides of carbon, ammonia (when the substance contained nitrogen), and other bodies. By this reaction ethyl alcohol C_2H_6O and acetic acid $C_2H_4O_2$ were converted into ethane C_2H_6; butyric acid $C_4H_8O_2$ and succinic acid $C_4H_6O_4$ yielded butane C_4H_{10}, whilst benzene C_6H_6 and phenol C_6H_6O were transformed into hexane C_6H_{14}. From wood, charcoal, and coal, a mixture of a great number of paraffins was obtained, but graphite underwent no change.

Paraffins also generally occur amongst the products of destructive distillation of organic substances, and are consequently found in wood tar and coal tar, chiefly in such which have been obtained from coal rich in hydrogen, as that known as boghead and cannel coal. Some kinds of petroleum, as for instance that now largely exported from Pennsylvania, consist chiefly of a mixture of paraffins, which may be isolated by treating the oils with sulphuric acid, and afterwards with fuming nitric acid, or a mixture of concentrated sulphuric acid and commercial nitric acid. All other compounds occurring besides paraffins in these oils will thus be removed, being either oxidized or converted into nitro compounds, which are either dissolved by the acids or are much less volatile than the hydrocarbons. The oils are now washed with water, dried over caustic potash, and rectified over sodium. The distillate now consists only of paraffins, which are separated by fractional distillation.

In the chapter on isomerism, it has already been mentioned that among the paraffins a great number of isomerides may exist. Those of which the constitution has been ascertained may be divided into the following four groups:—

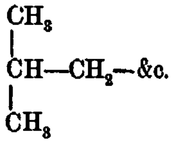
(1) *Normal Paraffins.*—The carbon atoms are linked together to a single chain, or no atom of carbon is united with more than two others, thus:—

$$C—C—C—C—\&c.$$

The following are known:—

		Boiling-point.			Boiling-point.
Methane . .	$C\ H_4$	gas	Hexane . .	$C_6\ H_{14}$	71°
Ethane . . .	$C_2\ H_2$	—	Heptane . .	$C_7\ H_{16}$	100
Propane . .	$C_3\ H_8$	—	Octane . . .	$C_8\ H_{18}$	125
Butane . . .	$C_4\ H_{10}$	+ 1°	Dodecane . .	$C_{12}H_{26}$	201
Pentane . .	$C_5\ H_{12}$	38	Hecdecane .	$C_{16}H_{34}$	278

(2) The paraffins of the second group are derived from propane by a single chain of carbon atoms being linked to the middle carbon atom:—

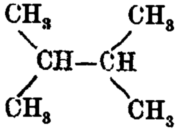


$$\begin{array}{l}CH_3\\ |\\ CH—CH_2—\&c.\\ |\\ CH_3\end{array}$$

The lowest member of this group contains, therefore, four atoms of carbon, and can be considered as marsh-gas in which three atoms of hydrogen have been replaced by methyl, and may therefore be called *trimethyl-methane.* The following are known:—

		Boiling-point.
Trimethyl-methane	$CH\left\{\begin{array}{l}CH_3\\CH_3\\CH_3\end{array}\right.$	− 15°
Dimethyl-ethyl-methane (Amyl Hydride)	$CH\left\{\begin{array}{l}CH_3\\CH_3\\C_2H_5\end{array}\right.$	+ 30
Dimethyl-propyl-methane (Ethyl-butyl)	$CH\left\{\begin{array}{l}CH_3\\CH_3\\C_3H_7\end{array}\right.$	62
Dimethyl-butyl-methane (Ethyl-amyl)	$CH\left\{\begin{array}{l}CH_3\\CH_3\\C_4H_9\end{array}\right.$	91

(3) The paraffins of the third group contain the group $CH_3—CH—CH_3$ twice, the lowest member being *tetramethyl-ethane*:—



The following belong to this group :—

		Boiling-point.
Tetramethyl-ethane (Di-isopropyl)	$C_2H_2(CH_3)_4$	58°
Tetramethyl-butane (Di-isobutyl)	$C_4H_6(CH_3)_4$	109
Tetramethyl-pentane (Amyl-isobutyl)	$C_5H_8(CH_3)_4$	132
Tetramethyl-hexane (Diamyl)	$C_6H_{10}(CH_3)_4$	158

(4) One atom of carbon is linked together with four others :—

		Boiling-point.
Tetramethyl-methane	$C(CH_3)_4$	9·5°
Trimethyl-ethyl-methane	$C\left\{\begin{matrix}(CH_3)_3\\C_2H_5\end{matrix}\right.$	45
Dimethyl-diethyl-methane	$C\left\{\begin{matrix}(CH_3)_2\\(C_2H_5)_2\end{matrix}\right.$	86

The paraffins found in coal naphtha and in American petroleum belong to the first group; besides these, petroleum contains smaller quantities of hydrocarbons belonging to other groups. Solid paraffins occur also in nature; thus attar of roses contains one which appears to be $C_{16}H_{34}$. Boghead coal, which on distillation yields a large quantity of liquid and solid paraffins, contains solid paraffin ready formed, which can be extracted by means of ether; and similar compounds are found in coal measures and other bituminous strata, forming .the minerals known as *fossil wax*, *ozocerite*, &c. Solid paraffin exists also in large quantities in Canadian petroleum and other kinds of rock oil.

COMPOUNDS OF MONAD RADICALS.

By substituting in a paraffin one atom of hydrogen by another element or radical, compounds are formed in which the residue of the hydrocarbons acts as a monad radical. These radicals have been called the *alcohol radicals*, as of their compounds the alcohols have been known longest, and they moreover generally serve as starting-points for the preparation of other compounds. The alcohols are hydroxides or compounds of the alcohol radicals with the monad group *hydroxyl* OH. Thus common alcohol $C_2H_5.OH$ may be looked upon as ethane in which one atom of hydrogen has been exchanged for OH, or may be considered as water in which one atom of hydrogen has been substituted by the monad radical ethyl :—

$$\left.\begin{matrix}H\\H\end{matrix}\right\}O \quad \text{Water} \qquad\qquad \left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O \quad \begin{matrix}\text{Ethyl Hydroxide or}\\\text{Ethyl Alcohol.}\end{matrix}$$

The alcohols have therefore a constitution analogous to that of the hydroxides of monad elements, such as potassium hydroxide KOH, and as by acting with an acid on the latter we get a potassium salt and water, so by treating an alcohol with an acid it yields a *compound* or *saline ether*, the alcohol radical replacing the hydrogen of the acid :—

$$C_2H_5.OH + HCl = H_2O + C_2H_5Cl \qquad \text{Ethyl Chloride.}$$

$$C_2H_5.OH + HNO_3 = H_2O + C_2H_5.NO_3 \qquad \text{Ethyl Nitrate.}$$

$$C_2H_5.OH + \left.\begin{matrix}H\\H\end{matrix}\right\}SO_4 = H_2O + \left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}SO_4 \qquad \text{Ethyl-sulphuric Acid.}$$

In a great number of other reactions the alcohols behave in a manner quite analogous to water, as the chemical properties of their radicals have much greater resemblance to those of hydrogen than to those of the metals. By acting with iodine and phosphorus upon water we obtain phosphorous acid and hydriodic acid or hydrogen iodide, whilst by the action of these elements on an alcohol the corresponding iodide is formed :—

$$P + 3I + 3H_2O = PO_3H_3 + HI$$

$$P + 3I + 3C_2H_5.OH = PO_3H_3 + 3C_2H_5I$$

Phosphorus trichloride and water yield phosphorous acid and hydrochloric acid, and by the action of the trichloride on alcohol ethyl phosphite is formed :—

$$PCl_3 + 3H_2O = PO_3H_3 + 3HCl$$

$$PCl_3 + 3C_2H_5.OH = PO_3(C_2H_5)_3 + 3HCl$$

The alkali-metals act violently upon the alcohols, hydrogen being given off, and a mixed oxide or an alcohol, in which one atom of hydrogen has been replaced by the metal, being formed :—

$$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O + Na = \left.\begin{matrix}C_2H_5\\Na\end{matrix}\right\}O + H$$

By acting upon this compound with ethyl iodide the metal is replaced by ethyl, and we obtain *ethyl oxide* or *diethyl ether* :—

$$\left.\begin{matrix}C_2H_5\\Na\end{matrix}\right\}O + \left\{\begin{matrix}I\\C_2H_5\end{matrix}\right. = \left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O + \left\{\begin{matrix}I\\Na\end{matrix}\right.$$

By using the iodide of other alcohol radicals *mixed ethers* are formed, as $\left.\begin{matrix}CH_3\\C_2H_5\end{matrix}\right\}O$.

The oxygen of the alcohols or the ethers may be substituted by dyad sulphur; such compounds are formed by acting with alkaline sulphides upon the chlorides of the alcohol radicals :—

$$C_2H_5Cl + \left.\begin{matrix}H\\K\end{matrix}\right\}S = KCl + \left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}S$$

$$2C_2H_5Cl + \left.\begin{matrix}K\\K\end{matrix}\right\}S = 2KCl + \left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}S$$

But the analogy between hydrogen and the alcohol radicals appears most striking when the latter replace hydrogen in ammonia. The compound ammonias or *amines* thus formed are volatile bodies, possessing an ammoniacal smell, having a strong alkaline reaction, and combining with acids like ammonia. The amines are obtained by heating the iodides of the alcohol radicals with ammonia :—

$$C_2H_5I + \left.\begin{matrix}H\\H\\H\end{matrix}\right\}N = HI + \overset{\text{Ethylamine.}}{\left.\begin{matrix}C_2H_5\\H\\H\end{matrix}\right\}N}$$

By acting again upon ethylamine with ethyl iodide a second atom of hydrogen is replaced by ethyl :—

$$C_2H_5I + \left.\begin{matrix}C_2H_5\\H\\H\end{matrix}\right\}N = HI + \overset{\text{Diethylamine.}}{\left.\begin{matrix}C_2H_5\\C_2H_5\\H\end{matrix}\right\}N}$$

On subjecting diethylamine to the same reaction we obtain triethylamine $\left.\begin{matrix}C_2H_5\\C_2H_5\\C_2H_5\end{matrix}\right\}N$. Instead of substituting the three atoms of hydrogen in ammonia by one and the same radical, we may replace them by different radicals, and thus obtain mixed amines, as methyl-ethyl-amylamine $\left.\begin{matrix}CH_3\\C_2H_5\\C_5H_{11}\end{matrix}\right\}N$.

The triamines combine directly with iodides, just as ammonia combines with hydriodic acid. The compounds thus obtained are not decomposed by alkalis as the salts of the amines are, but are acted upon by moist oxide of silver, a hydroxide being formed :—

$$N(C_2H_5)_4I + \left.\begin{matrix}Ag\\H\end{matrix}\right\}O = \left.\begin{matrix}N(C_2H_5)_4\\H\end{matrix}\right\}O + AgI$$

Tetrethylammonium iodide yields tetrethylammonium hydroxide. These hydroxides are non-volatile solids and very soluble in water; they have a very strong alkaline reaction, and are as caustic as caustic potash, and give with metallic salts reactions like those of the caustic alkalis. Like the latter they neutralize acids, a salt and water being produced. The chlorides of these compound ammoniums, as well as the hydrochlorides of the amines, form crystalline double compounds with platinum tetrachloride and gold trichloride, corresponding to the double salts of potassium- and ammonium chloride, and their sulphates combine with aluminium sulphate, forming alums isomorphous with common alum.

The monamines are readily acted upon by nitrous acid; just as ammonium nitrite easily splits up into nitrogen and water, so a solution of ethylammonium nitrite (which may be obtained by decomposing the chloride with silver nitrite) yields on heating, nitrogen, ethyl alcohol, and water:—

$$N(C_2H_5)H_3.NO_2 = C_2H_5.OH + N_2 + H_2O$$

The other elements of the nitrogen group form compounds corresponding to the amines, &c.:—

Ethylphosphine.	Diethylphosphine.	Triethylphosphine.
$\left.\begin{matrix}C_2H_5\\H\\H\end{matrix}\right\}P$	$\left.\begin{matrix}C_2H_5\\C_2H_5\\H\end{matrix}\right\}P$	$\left.\begin{matrix}C_2H_5\\C_2H_5\\C_2H_5\end{matrix}\right\}P$
Trimethylarsine.	Triethylstibine.	Triethylbismuthine.
$\left.\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\right\}As$	$\left.\begin{matrix}C_2H_5\\C_2H_5\\C_2H_5\end{matrix}\right\}Sb$	$\left.\begin{matrix}C_2H_5\\C_2H_5\\C_2H_5\end{matrix}\right\}Bi$

Alcohol radicals can also be combined with several metals; these compounds correspond to the chlorides of the metals:—

$NaCl$	NaC_2H_5	Sodium Ethide
$Zn\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.$	$Zn\left\{\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right.$	Zinc Ethide
$Sn\left\{\begin{matrix}Cl\\Cl\\Cl\\Cl\end{matrix}\right.$	$Sn\left\{\begin{matrix}C_2H_5\\C_2H_5\\C_2H_5\\C_2H_5\end{matrix}\right.$	Stannic Ethide.

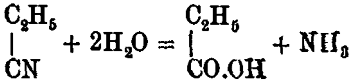
The compound ethers of the acids of cyanogen have a particular theoretical interest on account of each occurring in two isomeric forms.

By acting with silver cyanide upon ethyl iodide we obtain ethyl cyanide, a volatile liquid, which is acted upon by aqueous acids with the formation of ethylamine and formic acid. Ethyl cyanide or ethyl *carbamine* is also formed by acting with caustic potash upon a solution of ethylamine in chloroform CCl_3H. These reactions show that in these carbamines, the alcohol radical is combined with the nitrogen of cyanogen:—

$$(1)\ CN.C_2H_5 + 2H_2O = H_2N.C_2H_5 + CH_2O_2$$

$$(2)\ CCl_3H + H_2N.C_2H_5 = CN.C_2H_5 + 3HCl$$

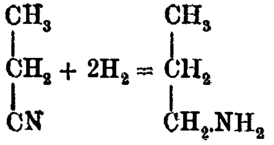
The carbamines are transformed by the action of heat into isomerides called *nitriles*, which are therefore always obtained when the metal in a metallic cyanide is replaced by an alcohol radical in a reaction taking place only at a high temperature. The nitriles are not acted upon by aqueous acids, but they are decomposed on heating them with alkalis, ammonia being formed and a fatty acid, containing one atom of carbon more than the alcohol radical. This reaction shows that the carbon of the cyanogen is combined with the alcohol radical. Thus the isomeric ethyl cyanide or *propionitrile* yields propionic acid:—



$$\begin{matrix} C_2H_5 \\ | \\ CN \end{matrix} + 2H_2O = \begin{matrix} C_2H_5 \\ | \\ CO.OH \end{matrix} + NH_3$$

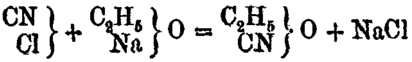
Whilst ethyl carbamine is still an ethyl compound, its isomeride propionitrile does not belong to this group; but is a derivative of propane C_3H_8, three atoms of hydrogen of this paraffin being replaced by nitrogen.

The nitriles combine with hydrogen in the nascent state, forming an amine. Thus propionitrile yields propylamine:—



$$\begin{matrix} CH_3 \\ | \\ CH_2 \\ | \\ CN \end{matrix} + 2H_2 = \begin{matrix} CH_3 \\ | \\ CH_2 \\ | \\ CH_2.NH_2 \end{matrix}$$

Ethyl Cyanate $\left.\begin{matrix} CN \\ C_2H_5 \end{matrix}\right\} O$ is formed by passing the vapour of cyanogen chloride into sodium ethylate:—



$$\left.\begin{matrix} CN \\ Cl \end{matrix}\right\} + \left.\begin{matrix} C_2H_5 \\ Na \end{matrix}\right\} O = \left.\begin{matrix} C_2H_5 \\ CN \end{matrix}\right\} O + NaCl$$

By the action of alkalis it is decomposed in the same manner as other compound ethers, alcohol and potassium cyanate being formed.

A body isomeric with ethyl cyanate is obtained by distilling a mixture of potassium cyanate and potassium ethyl sulphate. In this reaction most probably ethyl cyanate is first formed, which however, at the high temperature at which the reaction takes place, undergoes a molecular change, being converted into *ethyl carbimide* $N\left\{\begin{matrix} C_2H_5 \\ CO \end{matrix}\right.$. On heating this compound with caustic potash, we obtain ethylamine and carbon dioxide, which proves that the alcohol radical is combined with nitrogen:—

$$N\left\{\begin{matrix}C_2H_5\\CO\end{matrix}\right. + H_2O = N\left\{\begin{matrix}C_2H_5\\H_2\end{matrix}\right. + CO_2$$

The same kinds of isomerism occur amongst the ethers of sulphocyanic acid:—

$S\left\{\begin{matrix}C_2H_5\\CN\end{matrix}\right.$ Ethyl Sulphocyanate $N\left\{\begin{matrix}C_2H_5\\CS\end{matrix}\right.$ Ethyl Sulphocarbimide.

The first of these compounds yields, on treating it with caustic potash, potassium sulphocyanate and ethyl alcohol, whilst the second when heated with water forms ethylamine, carbon dioxide, and hydrogen sulphide:—

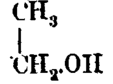
$$N\left\{\begin{matrix}C_2H_5\\CS\end{matrix}\right. + 2H_2O = N\left\{\begin{matrix}C_2H_5\\H_2\end{matrix}\right. + CO_2 + H_2S$$

The alcohols and their derivatives are divided into three very distinct groups.

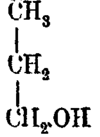
(1) PRIMARY ALCOHOLS AND FATTY ACIDS.

All paraffins contain the group CH_3 twice or more. By replacing one atom of hydrogen in one of these methyl groups by hydroxyl we obtain a *primary* alcohol:—

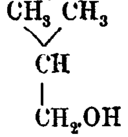
Ethyl Alcohol.



Propyl Alcohol.



Isobutyl Alcohol.



The most characteristic property of the primary alcohols is that by the moderate action of oxidizing agents, they first lose two atoms of hydrogen, a compound being formed called an *aldehyde* (alcohol dehydrogenatum). Ethyl alcohol yields acetaldehyde:—

$$C_2H_6O + O = C_2H_4O + H_2O$$

The aldehydes combine again with nascent hydrogen, being reconverted into alcohols, but they much more readily take up one atom of oxygen and form monobasic acids, which are compounds of monad oxygenated radicals, containing one atom of oxygen in place of two atoms of hydrogen in the alcohol radical:—

Ethyl Alcohol. Acetic Acid.

$$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O + O_2 = \left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O + H_2O$$

These monobasic acids have been called *fatty acids*, because many of them occur ready formed in different fats and oils. The hydroxyl of these acids can be replaced by the elements of the chlorine group. Thus by acting with phosphorus trichloride upon acetic acid, we obtain acetyl chloride:—

$$3\left(\left.\begin{matrix}C_2H_3O\\ \quad H\end{matrix}\right\}O\right) + PCl_3 = 3\left(\begin{matrix}C_2H_3O\\ \quad Cl\end{matrix}\right) + PO_3H_3$$

The chlorides of the acid radicals differ from those of the alcohol radicals by being less stable compounds; they are rapidly acted upon by water with the formation of the original fatty acid and hydrochloric acid.

The hydrogen in the hydroxyl group can also be replaced by alcohol radicals as well as by metals; the compounds thus formed are named *saline* or *compound* ethers. These ethers may be formed by different reactions. Thus ethyl acetate may be obtained—

(1) By heating potassium acetate with ethyl chloride:—

$$\left.\begin{matrix}C_2H_3O\\ \quad K\end{matrix}\right\}O + \left.\begin{matrix}Cl\\ C_2H_5\end{matrix}\right\} = \left.\begin{matrix}C_2H_3O\\ C_2H_5\end{matrix}\right\}O + \left.\begin{matrix}Cl\\ K\end{matrix}\right\}$$

(2) By acting upon ethyl alcohol with acetyl chloride:—

$$\left.\begin{matrix}C_2H_3O\\ \quad Cl\end{matrix}\right\} + \left.\begin{matrix}C_2H_5\\ \quad H\end{matrix}\right\}O = \left.\begin{matrix}C_2H_3O\\ C_2H_5\end{matrix}\right\}O + \left.\begin{matrix}H\\ Cl\end{matrix}\right\}$$

(3) By distilling a mixture of ethyl alcohol and sulphuric acid with potassium acetate:—

$$\left.\begin{matrix}C_2H_3O\\ \quad H\end{matrix}\right\}O + \left.\begin{matrix}C_2H_5\\ \quad H\end{matrix}\right\}O = \left.\begin{matrix}C_2H_3O\\ C_2H_5\end{matrix}\right\}O + H_2O$$

The oxides of the acid radicals, commonly called *anhydrides*, are also known. Thus we obtain acetyl oxide or acetic anhydride by acting with acetyl chloride upon potassium acetate:—

$$\left.\begin{matrix}C_2H_2O\\ \quad Cl\end{matrix}\right\} + \left.\begin{matrix}C_2H_3O\\ \quad Na\end{matrix}\right\}O = \left.\begin{matrix}C_2H_3O\\ C_2H_3O\end{matrix}\right\}O + NaCl$$

These anhydrides are readily acted upon by water, thus:—

$$\left.\begin{matrix}C_2H_3O\\ C_2H_3O\end{matrix}\right\}O + \left.\begin{matrix}H\\ H\end{matrix}\right\}O = \left.\begin{matrix}C_2H_3O\\ \quad H\end{matrix}\right\}O + \left.\begin{matrix}C_2H_3O\\ \quad H\end{matrix}\right\}O$$

By acting on fatty acids with phosphorus pentasulphide we obtain so-called thio-acids:—

$$5\left(\left.\begin{matrix}C_2H_3O\\ \quad H\end{matrix}\right\}O\right) + P_2S_5 = 5\left(\left.\begin{matrix}C_2H_3O\\ \quad H\end{matrix}\right\}S\right) + P_2O_5$$

These thio-acids are also monobasic, and form salts, saline ethers, anhydrides, &c.:—

$$\left.\begin{matrix}C_2H_3O\\ \quad K\end{matrix}\right\}S \quad \text{Potassium Thiacetate}$$

$\left.\begin{matrix}C_2H_3O\\C_2H_5\end{matrix}\right\}S$ Ethyl Thiacetate

$\left.\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\right\}S$ Thiacetic Anhydride or Acetyl Sulphide

The acid radicals can also replace hydrogen in ammonia and in the amines; such compound ammonias are called *amides*:—

Acet-amide $\left.\begin{matrix}C_2H_3O\\H\\H\end{matrix}\right\}N$ Diacet-amide $\left.\begin{matrix}C_2H_3O\\C_2H_3O\\H\end{matrix}\right\}N$ Ethyl-diacetamide $\left.\begin{matrix}C_2H_3O\\C_2H_3O\\C_2H_5\end{matrix}\right\}N$

In a great number of reactions the fatty acids are decomposed in such a manner that one atom of carbon is separated from the molecule. We have already seen that by electrolysis acetic acid splits up into hydrogen, carbon dioxide, and methyl, which latter in the nascent state combines with another methyl to form ethane:—

$$2\left(\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O\right) = 2\,CO_2 + H_2 + \left\{\begin{matrix}CH_3\\CH_3\end{matrix}\right.$$

By the same reaction butyric acid $C_4H_8O_2$ yields hexane C_6H_{14}:—

$$2\left(\left.\begin{matrix}C_4H_7O\\H\end{matrix}\right\}O\right) = 2\,CO_2 + H_2 + \left\{\begin{matrix}C_3H_7\\C_3H_7\end{matrix}\right.$$

On heating a mixture of sodium acetate and caustic soda, marsh-gas is formed:—

$$\left.\begin{matrix}C_2H_3O\\Na\end{matrix}\right\}O + \left.\begin{matrix}Na\\H\end{matrix}\right\}O = CH_4 + Na_2CO_3$$

On the other hand, any fatty acid can be built up synthetically from an alcohol containing one atom of hydrogen less.

Sodium methide combines directly with carbon dioxide, forming sodium acetate:—

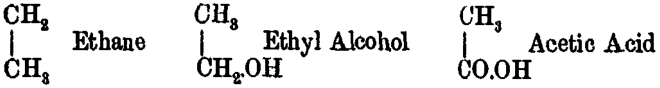
$$NaCH_3 + CO_2 = NaC_2H_3O_2$$

By combining cyanogen with methyl we obtain, as already explained, acetonitrile, which on heating with caustic potash yields ammonia and potassium acetate:—

$$\begin{matrix}CH_3\\|\\CN\end{matrix} + KOH + H_2O = \begin{matrix}CH_3\\|\\CO_2K\end{matrix} + NH_3$$

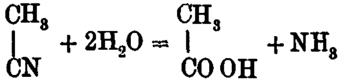
From all these different decompositions and formations of acetic acid it appears that it contains the group CH_3, and we can explain all these reactions by giving to acetic acid the rational formula $\left.\begin{matrix}CH_3.CO\\H\end{matrix}\right\}O$, being a compound of methyl with the monad group $\left.\begin{matrix}CO\\H\end{matrix}\right\}O$ or $\begin{matrix}C{=}O,\\|\\OH\end{matrix}$ which has been called *carboxyl* or *oxatyl*. This compound radical is present in most of the organic acids, and the basicity of an acid depends on the number of times it occurs. Thus the fatty acids are compounds of carboxyl with monad alcohol radicals, their general formula being $\left.\begin{matrix}C_nH_{2n+1}CO\\H\end{matrix}\right\}O$.

The group carboxyl is derived from methyl by oxidation:—



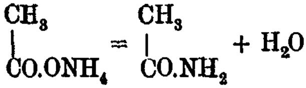
$$\begin{array}{l}CH_3\\|\\CH_3\end{array}\ \text{Ethane}\qquad\begin{array}{l}CH_3\\|\\CH_2.OH\end{array}\ \text{Ethyl Alcohol}\qquad\begin{array}{l}CH_3\\|\\CO.OH\end{array}\ \text{Acetic Acid}$$

Carboxyl is also, as we have already seen, easily derived from cyanogen, which by the action of alkalis takes up water and forms ammonia and carboxyl:—



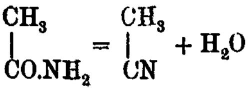
$$\begin{array}{l}CH_3\\|\\CN\end{array}+2H_2O=\begin{array}{l}CH_3\\|\\CO\,OH\end{array}+NH_3$$

On the other hand, carboxyl can again be reconverted to cyanogen; by heating ammonium acetate, it decomposes into water and acetamide:—



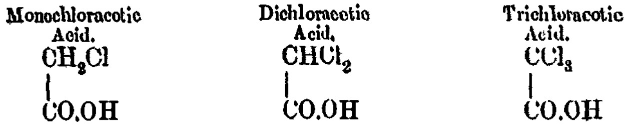
$$\begin{array}{l}CH_3\\|\\CO.ONH_4\end{array}=\begin{array}{l}CH_3\\|\\CO.NH_2\end{array}+H_2O$$

And on distilling acetamide with phosphorus pentoxide another molecule of water is taken out and acetonitrile is formed:—



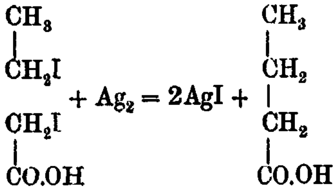
$$\begin{array}{l}CH_3\\|\\CO.NH_2\end{array}=\begin{array}{l}CH_3\\|\\CN\end{array}+H_2O$$

By acting on fatty acids with chlorine, substitution takes place in the alcohol radical; thus from acetic acid the following three chlorinated acids have been obtained:—



$$\begin{array}{ccc}\text{Monochloracetic Acid.} & \text{Dichloracetic Acid.} & \text{Trichloracetic Acid.}\\ \begin{array}{l}CH_2Cl\\|\\CO.OH\end{array} & \begin{array}{l}CHCl_2\\|\\CO.OH\end{array} & \begin{array}{l}CCl_3\\|\\CO.OH\end{array}\end{array}$$

In the place of chlorine we may also introduce bromine or iodine, and these elements can again be exchanged by other monad radicals. By replacing them by alcohol radicals we obtain higher members of the series of fatty acids; thus, by heating iodacetic acid with ethyl iodide and finely divided silver, butyric acid is formed:—



$$\begin{array}{l}CH_3\\|\\CH_2I\\\\CH_2I\\|\\CO.OH\end{array} + Ag_2 = 2AgI + \begin{array}{l}CH_3\\|\\CH_2\\|\\CH_2\\|\\CO.OH\end{array}$$

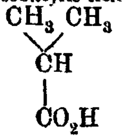
If we act upon the compound ether of a fatty acid with sodium, hydrogen is replaced by the metal; thus ethyl acetate yields as the first product of the reaction *sodacetic ether* $\begin{array}{l}CH_2Na\\|\\CO.OC_2H_5.\end{array}$

By treating this compound with ethyl iodide the ethyl and sodium change places, and the ethyl ether of *ethyl-acetic acid* or *butyric acid* is formed.

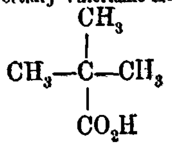
It will be easily understood how, by employing other alcoholic iodides, the whole series of the fatty acids may be built up synthetically.

By the further action of sodium upon sodacetic ether the compounds $\begin{array}{l}CHNa_2\\|\\CO.OC_2H_5\end{array}$ and $\begin{array}{l}CNa_3\\|\\CO.OC_2H_5\end{array}$ are formed, which are acted upon by the iodides of the alcohol radicals in the same manner as sodacetic ether. Thus by treating them with methyl iodide disodacetic ether yields the ethyl ether of *dimethyl-acetic* or *isobutyric acid*, and trisodacetic ether gives the ethyl compound of *trimethyl-acetic* or tertiary valerianic acid:—

Isobutyric Acid.



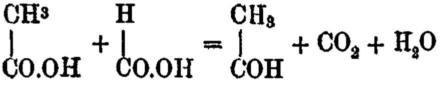
Tertiary Valerianic Acid.



$$\begin{array}{c}CH_3\\|\\CH_3—C—CH_3\\|\\CO_2H\end{array}$$

All fatty acids can be again reduced to the alcohols from which they are derived by oxidation.

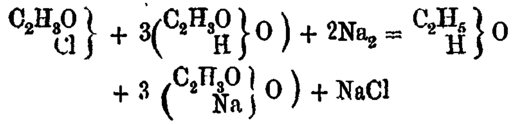
(1) By distilling an intimate mixture of dry calcium formate with the calcium salt of a fatty acid, the aldehyde of the latter is produced:—



$$\begin{array}{l}CH^3\\|\\CO.OH\end{array} + \begin{array}{l}H\\|\\CO.OH\end{array} = \begin{array}{l}CH_3\\|\\COH\end{array} + CO_2 + H_2O$$

The aldehydes combine readily with nascent hydrogen, as we have already seen, and are converted into alcohols.

(2) On acting on a mixture of an acid and its chloride with sodium amalgam the chlorine is replaced by hydrogen, and the aldehyde thus formed combines with a molecule of hydrogen:—



$$\left.\begin{matrix}C_2H_3O\\Cl\end{matrix}\right\} + 3\left(\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O\right) + 2Na_2 = \left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O + 3\left(\left.\begin{matrix}C_2H_3O\\Na\end{matrix}\right\}O\right) + NaCl$$

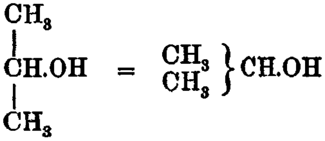
The following table contains all the primary alcohols and fatty acids which have been more closely studied :—

SERIES OF PRIMARY ALCOHOLS.			SERIES OF FATTY ACIDS.		
		Boiling-point.			Boiling-point.
Methyl Alcohol	CH_4O	66°	Formic Acid	CH_2O_2	100°
Ethyl „	C_2H_6O	78·4	Acetic „	$C_2H_4O_2$	118
Propyl „	C_3H_8O	97	Propionic „	$C_3H_6O_2$	141
Butyl „	$C_4H_{10}O$	116	Butyric „	$C_4H_8O_2$	163
Pentyl „	$C_5H_{12}O$	137	Pentylic „	$C_5H_{10}O_2$	185
Hexyl „	$C_6H_{14}O$	157	Hexylic „	$C_6H_{12}O_2$	205
Heptyl „	$C_7H_{16}O$	176	Heptylic „	$C_7H_{14}O_2$	224
Octyl „	$C_8H_{18}O$	195	Octylic „	$C_8H_{16}O_2$	233
			Nonylic „	$C_9H_{18}O_2$	254
Isobutyl Alcohol	$C_4H_{10}O$	109°	Isobutyric Acid	$C_4H_8O_2$	153°
Amyl „	$C_5H_{12}O$	132	Valerianic „	$C_5H_{10}O_2$	175
Isohexyl „	$C_6H_{14}O$	150	Isohexylic „	$C_6H_{12}O_2$	199
Isoheptyl „	$C_7H_{16}O$	165	Isoheptylic „	$C_7H_{14}O_2$	212
		Melting-point.			Melting-point.
			Capric Acid	$C_{10}H_{20}O_2$	30°
			Lauric „	$C_{12}H_{24}O_2$	43·6
			Myristic „	$C_{14}H_{28}O_2$	53·8
Cetyl Alcohol	$C_{16}H_{34}O$	50°	Palmitic „	$C_{16}H_{32}O_2$	62
			Stearic „	$C_{18}H_{36}O_2$	69·2
			Arachidic „	$C_{20}H_{40}O_2$	75
			Behenic „	$C_{22}H_{44}O_2$	76
Ceryl „	$C_{27}H_{56}O$	79	Cerotic „	$C_{27}H_{54}O_2$	78
Melissyl „	$C_{30}H_{62}O$	85	Melissic „	$C_{30}H_{60}O_2$	80

The alcohols and acids forming the first group contain the carbon-atoms linked together in a single chain, and are called normal compounds, whilst those constituting the second group have the carbon-atoms arranged in the same way as in the second group of the paraffins. The constitution of the members of the third group, which all occur ready formed in nature, is not yet exactly known.

(2) SECONDARY ALCOHOLS AND KETONES.

In the secondary alcohols the group OH is linked to a carbon atom, itself combined with two other atoms of carbon. The lowest member in the series contains consequently three atoms of carbon, and is the secondary propyl alcohol or *dimethyl carbinol*:—



$$\begin{array}{l} CH_3 \\ | \\ CH.OH \\ | \\ CH_3 \end{array} = \left.\begin{array}{l} CH_3 \\ CH_3 \end{array}\right\} CH.OH$$

This body may be regarded as methyl alcohol in which two hydrogen atoms are substituted by methyl, and has therefore received the name dimethyl carbinol, the term carbinol being used for methyl alcohol in order to avoid such cumbrous terms as dimethylated methyl alcohol, &c.

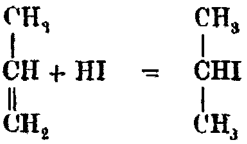
Secondary alcohols are formed by several general reactions:—

(1) On acting with chlorine upon the paraffins there is always a mixture of a primary and a secondary chloride formed at the same time.

(2) All alcohols of polygenic radicals yield, on heating them with an excess of concentrated hydriodic acid, secondary iodides. Thus mannite $C_6H_8(OH)_6$ is converted by this reaction into a secondary hexyl iodide:—

$$C_6H_8(OH)_6 + 11HI = C_6H_{13}I + 6H_2O + 5I_2$$

(3) The hydrocarbons of the series C_nH_{2n} combine directly with the hydracids forming secondary chlorides, bromides, or iodides:—

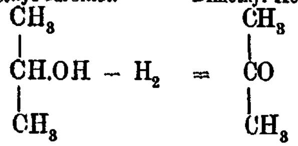


$$\begin{array}{l} CH_3 \\ | \\ CH + HI \\ \| \\ CH_2 \end{array} = \begin{array}{l} CH_3 \\ | \\ CHI \\ | \\ CH_3 \end{array}$$

From these chlorides, &c., the alcohols are obtained by the same reactions by which the primary chlorides are converted into alcohols.

The secondary alcohols, as well as their haloid ethers, differ from the primary compounds by being much more easily resolved into an olefine and water or a hydracid. Both groups, however, are most readily distinguished by their products of oxidation. The secondary alcohols lose in the first instance, like the primary alcohols, two atoms of hydrogen, but the compound thus formed is not an aldehyde but an *acetone* or *ketone*:—

Dimethyl Carbinol. Dimethyl Ketone.



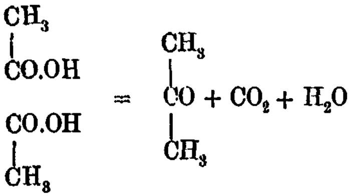
$$\begin{array}{l}CH_3\\ |\\ CH.OH\\ |\\ CH_3\end{array} - H_2 = \begin{array}{l}CH_3\\ |\\ CO\\ |\\ CH_3\end{array}$$

The ketones contain two alcohol radicals combined with carbonyl; they may be obtained by different other reactions besides the oxidation of secondary alcohols.

(1) By the action of the zinc compounds of the alcohol radicals upon the chlorides of the fatty acids. Thus zinc methide and acetyl chloride yield dimethyl carbinol, and by acting upon the same chloride with zinc ethide, methyl-ethyl ketone is produced:—

$$Zn\left\{\begin{array}{l}C_2H_5\\ C_2H_5\end{array}\right. + 2\left\{\begin{array}{l}Cl\\ CO\\ CH_3\end{array}\right. = 2\left\{\begin{array}{l}C_2H_5\\ CO\\ CH\end{array}\right. + ZnCl_2$$

(2) Ketones are also formed by the destructive distillation of the calcium- and other salts of fatty acids, or by passing the vapours of these acids through a red-hot tube:—



$$\begin{array}{l}CH_3\\ |\\ CO.OH\\ \\ CO.OH\\ |\\ CH_3\end{array} = \begin{array}{l}CH_3\\ |\\ CO\\ |\\ CH_3\end{array} + CO_2 + H_2O$$

The ketones are capable of combining with nascent hydrogen like the aldehydes, a secondary alcohol being again formed; but on further oxidation they do not yield like the aldehydes an acid containing the same number of carbon atoms, but the molecule is broken up into two fragments according to the following law. The most simple alcohol radical remains combined with the carboxyl and forms a fatty acid, whilst the other alcohol radical is oxidized exactly in the same way as the alcohol corresponding to it would be. Thus *dimethyl ketone* $\left.\begin{array}{l}CH_3\\ CH_3\end{array}\right\}CO$ yields acetic acid and formic acid (or carbon dioxide); *methyl-ethyl ketone* $\left.\begin{array}{l}CH_3\\ C_2H_5\end{array}\right\}CO$ yields only acetic acid, and *diethyl ketone* $\left.\begin{array}{l}C_2H_5\\ C_2H_5\end{array}\right\}CO$ acetic and propionic acids, and the same two acids are obtained from *methyl-propyl ketone* $\left.\begin{array}{l}CH_3\\ C_3H_7\end{array}\right\}CO$, whilst *methyl-isopropyl ketone* $\left.\begin{array}{l}CH_3\\ (CH_3)_2CH\end{array}\right\}CO$ is first resolved into acetic acid and dimethyl ketone, which latter is then further oxidized as stated above.

The constitution of a secondary alcohol, as well as a ketone, can therefore be easily ascertained by examining their products of oxidation. Thus the secondary hexyl alcohol from mannite was found to be *methyl-butyl carbinol* $\left.\begin{matrix}CH_3\\C_4H_9\end{matrix}\right\}CH.OH$; for it yields on oxidation first a ketone, which on further oxidation is resolved into acetic and butyric acids.

The following table contains the secondary alcohols which have so far been prepared:—

		Boiling point.
Dimethyl Carbinol	$\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\}CH.OH$	84°
Methyl-ethyl Carbinol	$\left.\begin{matrix}CH_3\\C_2H_5\end{matrix}\right\}CH.OH$	97
Methyl-isopropyl Carbinol	$\left.\begin{matrix}CH_3\\(CH_3)_2CH\end{matrix}\right\}CH.OH$	108
Methyl-propyl Carbinol	$\left.\begin{matrix}CH_3\\C_3H_7\end{matrix}\right\}CH.OH$	120
Methyl-butyl Carbinol	$\left.\begin{matrix}CH_3\\C_4H_9\end{matrix}\right\}CH.OH$	136
Methyl-amyl Carbinol	$\left.\begin{matrix}CH_3\\(CH_3)_2C_3H_5\end{matrix}\right\}CH.OH$	147
Methyl-pentyl Carbinol	$\left.\begin{matrix}CH_3\\C_5H_{11}\end{matrix}\right\}CH.OH$	160
Methyl-hexyl Carbinol	$\left.\begin{matrix}CH_3\\C_6H_{13}\end{matrix}\right\}CH.OH$	181
Methyl-nonyl Carbinol	$\left.\begin{matrix}CH_3\\C_9H_{19}\end{matrix}\right\}CH.OH$	229

(3) TERTIARY ALCOHOLS.

In these alcohols the hydroxyl is combined with a carbon atom itself linked to three others, the lowest member of the group being trimethyl carbinol or tertiary butyl alcohol $(CH_3)_3C.OH$. Tertiary alcohols are formed by one general reaction, viz. the action of the chlorides of the fatty acids upon the zinc compounds of the alcohol radicals. As we have already seen, acetones are formed by acting with two molecules of these chlorides upon one molecule of the zinc compound, but when an excess of the latter is employed the acetone combines with it just as it combines with one molecule of hydrogen. Thus on adding an excess of zinc methide to acetyl chloride we obtain the compound $\left.\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\right\}CO.ZnCH_3$, which is decomposed by water with the formation of trimethyl carbinol, marsh-gas, and zinc hydroxide:—

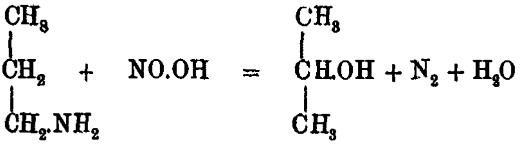
$$\left.\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\right\}CO.ZnCH_3 + 2H_2O = \left.\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\right\}C.OH + CH_4 + Zn(OH)_2$$

The oxidation of tertiary alcohols takes place according to a law similar to that which rules the oxidation of the ketones; the most simple alcohol radical remaining combined with the carbon-atom by which the whole group is kept together, whilst the two other radicals are oxidized separately.

The following tertiary alcohols are known:—

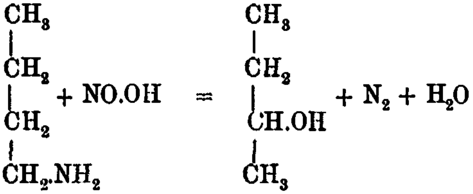
		Boiling-point.
Trimethyl Carbinol	$\left.\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\right\}C.OH$	82°
Dimethyl-ethyl Carbinol	$\left.\begin{matrix}CH_3\\CH_3\\C_2H_5\end{matrix}\right\}C.OH$	100
Dimethyl-isopropyl Carbinol	$\left.\begin{matrix}CH_3\\CH_3\\(CH_3)_2CH\end{matrix}\right\}C.OH$	112
Dimethyl-propyl Carbinol	$\left.\begin{matrix}CH_3\\CH_3\\C_3H_7\end{matrix}\right\}C.OH$	115
Methyl-diethyl Carbinol	$\left.\begin{matrix}CH_3\\C_2H_5\\C_2H_5\end{matrix}\right\}C.OH$	120
Triethyl Carbinol	$\left.\begin{matrix}C_2H_5\\C_2H_5\\C_2H_5\end{matrix}\right\}C.OH$	140
Diethyl-propyl Carbinol	$\left.\begin{matrix}C_2H_5\\C_2H_5\\C_3H_7\end{matrix}\right\}C.OH$	—

A very singular reaction must be mentioned here by which normal primary alcohols may be converted into iso-alcohols, secondary, and tertiary alcohols. This general method consists in heating the hydrochlorides of the amines with silver nitrite and water. Thus when normal propylamine is submitted to this reaction it is converted into secondary propyl alcohol:—

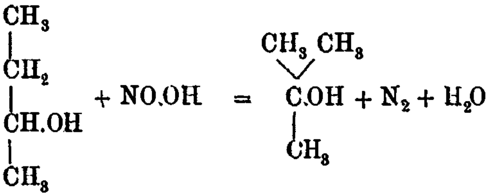


$$\begin{array}{l} CH_3 \\ | \\ CH_2 \\ | \\ CH_2.NH_2 \end{array} + NO.OH = \begin{array}{l} CH_3 \\ | \\ CH.OH \\ | \\ CH_3 \end{array} + N_2 + H_2O$$

By the same reaction primary normal butylamine is transformed into isobutyl alcohol, and isobutylamine into tertiary butyl alcohol:—



$$\begin{array}{l} CH_3 \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CH_2.NH_2 \end{array} + NO.OH = \begin{array}{l} CH_3 \\ | \\ CH_2 \\ | \\ CH.OH \\ | \\ CH_3 \end{array} + N_2 + H_2O$$



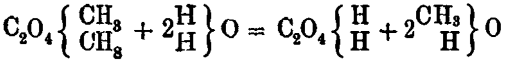
$$\begin{array}{l} CH_3 \\ | \\ CH_2 \\ | \\ CH.OH \\ | \\ CH_3 \end{array} + NO.OH = \begin{array}{l} CH_3\ CH_3 \\ \ \ \diagdown\diagup \\ \ \ C.OH \\ \ \ | \\ \ \ CH_3 \end{array} + N_2 + H_2O$$

The action of nitrous acid on the monamines may thus be described as always producing the alcohol of a radical containing one more methyl group than the original amine, provided the amine be capable of forming an isomeride containing one more methyl; thus tertiary butylamine cannot contain more than three methyl-groups, and yields, therefore, by the above reaction again the tertiary alcohol.

METHYL COMPOUNDS.

Methyl Alcohol $CH_3.OH$.—This compound, commonly called wood spirit (*μέθυ* wine, *ὕλη* wood), occurs amongst the products of the destructive distillation of wood, forming about one per cent. of the aqueous distillate. To isolate it, the liquid, which contains a large quantity of acetic acid, is distilled, and the first portion of the distillate, consisting of aqueous methyl alcohol mixed with other volatile bodies, such as methyl acetate, acetone, dimethyl acetal, and empyreumatic oils, is rectified over quicklime. On adding anhydrous calcium chloride to the liquid, heat is evolved, the methyl alcohol combining with the calcium chloride forming a solid crystalline compound, whilst the other bodies present remain as an oily layer which is poured off, the last traces of these being removed by heating the solid mass to 100°, at which temperature the compound is not decomposed. The dry residue yields, on distillation with water, aqueous methyl alcohol, which is dried over quicklime and again distilled from a water bath.

The alcohol thus obtained is not quite pure. To prepare the pure compound, purified wood spirit is carefully mixed with its own weight of sulphuric acid, two parts of potassium binoxalate are added, and the mixture distilled. As soon as crystals of methyl oxalate appear in the neck of the retort, the receiver is changed and the distillation continued as long as this compound comes over. These crystals are finely powdered, pressed between filter paper, and dried over sulphuric acid. On distilling the pure ether with water it splits up into methyl alcohol and oxalic acid :—



$$C_2O_4\left\{\begin{matrix}CH_3\\CH_3\end{matrix} + 2\begin{matrix}H\\H\end{matrix}\right\}O = C_2O_4\left\{\begin{matrix}H\\H\end{matrix} + 2\begin{matrix}CH_3\\H\end{matrix}\right\}O$$

The dilute methyl alcohol thus obtained is distilled from a water bath, to remove the greater part of the water, dried over quicklime, and rectified.

The winter-green oil from *Gaultheria procumbens*, a plant indigenous to North America, consists chiefly of the methyl ether of salicylic acid. On distilling this oil with caustic potash pure methyl alcohol is obtained.

Methyl alcohol is a colourless, mobile liquid, possessing a pure spirituous smell; its specific gravity is 0·8142 at 0°, and it boils at 66°. It burns with a bluish non-luminous flame, and is miscible with water in all proportions. With caustic baryta and with calcium chloride it forms crystalline compounds which are decomposed by water.

Methyl alcohol is used instead of spirits of wine as a solvent for resins, essential oils, &c., for heating purposes, and in the manufacture of aniline colours.

On oxidation it is converted into formic acid; this acid is also formed by passing the vapour over heated soda-lime :—

$$CH_3.OH + NaOH = CHO.ONa + 2H_2$$

Potassium and sodium dissolve in methyl alcohol with the evolution of hydrogen. On cooling, the compounds $CH_3.OK$ or $CH_3.ONa$ crystallize out, which are decomposed by water, methyl alcohol and caustic alkali being formed.

Methyl Chloride CH_3Cl is obtained by heating a mixture of one part of methyl alcohol and three parts of sulphuric acid with two parts of common salt :—

$$CH_3.OH + NaCl + H_2SO_4 = CH_3Cl + NaHSO_4 + H_2O$$

It is a colourless gas, possessing an ethereal smell. When exposed to a low temperature it is condensed to a mobile liquid, boiling at

– 21°. It burns with a fine green flame, like most organic chlorine compounds. On heating it for some time in closed vessels with caustic potash to 100° methyl alcohol is formed:—

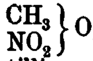
$$CH_3Cl + KOH = CH_3.OH + KCl$$

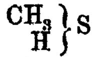
Methyl Bromide CH_3Br is formed by acting on methyl alcohol with phosphorus and bromine. It is a colourless liquid, heavier than water, and boiling at + 13°.

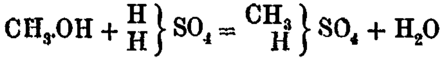
Methyl Iodide CH_3I.—To prepare this compound 100 parts of iodine are gradually added to a mixture of thirty-five parts of purified wood spirit and ten parts of amorphous phosphorus. After standing for some hours the methyl iodide is distilled off:—

$$5CH_3.OH + 5I + P = 5CH_3I + H_3PO_4 + H_2O$$

Methyl iodide is a colourless liquid with the specific gravity 2·2 at 0°. It boils at 43°, and possesses a peculiar smell somewhat resembling that of garlic. Like other alcoholic iodides it becomes brown when exposed to light and air by the separation of free iodine. It is used in the manufacture of aniline violets and green.

Methyl Nitrate  $\left.\begin{matrix}CH_3\\NO_2\end{matrix}\right\}O$, a colourless liquid with a pleasant smell, is obtained by distilling a mixture of methyl alcohol, saltpetre, and sulphuric acid. It boils at 66°, and its vapour, when heated to 150°, decomposes with a violent explosion. It is also used in the manufacture of aniline colours.

Methylsulphuric Acid  $\left.\begin{matrix}CH_3\\H\end{matrix}\right\}SO_4$.—On mixing methyl alcohol with concentrated sulphuric acid much heat is evolved, the following reaction taking place:—



$$CH_3.OH + \left.\begin{matrix}H\\H\end{matrix}\right\}SO_4 = \left.\begin{matrix}CH_3\\H\end{matrix}\right\}SO_4 + H_2O$$

To obtain the pure compound the mixture, which contains some free methyl alcohol and an excess of sulphuric acid, is diluted with water, and carefully neutralized in the cold with freshly precipitated barium carbonate, and the filtrate evaporated at a low temperature to obtain the barium salt of the monobasic methylsulphuric acid, which forms colourless crystals having the composition $(CH_3)_2(SO_4)_2Ba + 2H_2O$. On adding dilute sulphuric acid to the aqueous solution of this salt until all the barium is precipitated, a solution of the free methylsulphuric acid is obtained, which on evaporation *in vacuo* crystallizes in white needles which are readily soluble in water, forming a strongly acid solution.

Methyl Sulphate $(CH_3)_2SO_4$ is produced by distilling a mixture of one part of methyl alcohol and eight parts of sulphuric acid. It is a colourless liquid, smelling like leek, and boiling at 188°. On heating it with water it yields methyl alcohol and methylsulphuric acid.

Dimethyl Ether or Methyl Oxide $\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\}O$. — This compound is formed by the action of methyl alcohol on methylsulphuric acid:—

$$\left.\begin{matrix}CH_3\\H\end{matrix}\right\}O + \left.\begin{matrix}CH_3\\H\end{matrix}\right\}SO_4 = \left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\}O + \left.\begin{matrix}H\\H\end{matrix}\right\}SO_4$$

To prepare it methyl alcohol is distilled with four times its weight of sulphuric acid, whilst by using a larger quantity of the acid an exchange occurs in the opposite direction, methyl sulphate and water being produced.

Dimethyl ether is a colourless gas, smelling like common ether; it can be condensed to a liquid, boiling at $-21°$, and combines with sulphur trioxide, forming methyl sulphate:—

$$\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\}O + SO_3 = \left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\}SO_4$$

METHYL CYANIDES.

Methyl Cyanide or Methyl Carbamine $CN.CH_3$.—To obtain this compound two molecules of silver cyanide and one molecule of methyl iodide diluted with some ether are heated together for some hours in sealed tubes. The products of the reaction consist of silver iodide and a crystalline double compound $CN.CH_3 + AgCN$, which is decomposed on distilling it with potassium cyanide and water.

Methyl carbamine is a colourless liquid, boiling at 58° and possessing a most penetrating, unbearable smell; the inhalation of its vapour produces a bitter taste in the mouth and deep down in the throat. In larger quantities it causes giddiness, nausea, and headache. Water acts on it slowly, more quickly, however, in presence of acids, formic acid and methylamine being formed:—

$$CN.CH_3 + 2H_2O = H_2N.CH_3 + CH_2O_2$$

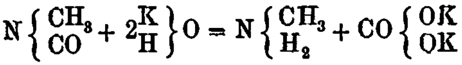
On heating it gently with mercuric oxide, different products are formed, amongst which methyl carbimide is found:—

$$N\left\{\begin{matrix}CH_3\\C\end{matrix}\right. + HgO = N\left\{\begin{matrix}CH_3\\CO\end{matrix}\right. + Hg$$

Acetonitrile $\left\{\begin{matrix}CH_2\\CN\end{matrix}\right.$.—On distilling a mixture of potassium cyanide and potassium methylsulphate, only a small quantity of methyl carbamine is obtained, the greater portion undergoing a molecular change, and forming the isomeric nitrile, a colourless liquid, boiling at 77°, and possessing a penetrating but not disagreeable smell. It is not acted upon by dilute acids, but on heating it with a solution of caustic potash it yields ammonia and potassium acetate:—

$$CH_3.CN + KOH + H_2O = \left.\begin{matrix}CH_3.CO\\K\end{matrix}\right\}O + NH_3$$

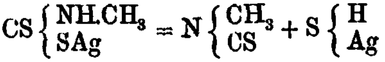
Methyl Carbimide $N\left\{\begin{matrix}CH_3\\CO\end{matrix}\right.$ is obtained by distilling a mixture of potassium cyanate and potassium methylsulphate. It is a colourless, very volatile liquid, having a very pungent and irritating smell. This body has for a long time been regarded as methyl cyanate, a compound which is not known; on heating it with caustic potash it does not yield potassium cyanate and methyl alcohol, as would be the case if it were a cyanic ether, but it gives potassium carbonate and methylamine:—



$$N\left\{\begin{matrix}CH_3\\CO\end{matrix}\right. + 2\left.\begin{matrix}K\\H\end{matrix}\right\}O = N\left\{\begin{matrix}CH_3\\H_2\end{matrix}\right. + CO\left\{\begin{matrix}OK\\OK\end{matrix}\right.$$

Methyl Sulphocyanate $\left.\begin{matrix}CH_3\\CN\end{matrix}\right\}S$, a colourless liquid, boiling at 133°, and smelling like leek, is produced by the distillation of potassium sulphocyanate with potassium methyl sulphate.

Methyl Sulphocarbimide $N\left\{\begin{matrix}CH_3\\CS\end{matrix}\right.$.—Methylamine combines with carbon disulphide, forming *methyl-sulphocarbonic acid* $CS\left\{\begin{matrix}NH.CH_3\\SH\end{matrix}\right.$. On heating the silver salt of this acid with water, the following decomposition occurs:—



$$CS\left\{\begin{matrix}NH.CH_3\\SAg\end{matrix}\right. = N\left\{\begin{matrix}CH_3\\CS\end{matrix}\right. + S\left\{\begin{matrix}H\\Ag\end{matrix}\right.$$

Methyl sulphocarbimide forms white crystals, melting at 34° and boiling at 119°; its odour is pungent, and resembles that of horseradish. The sulphocarbimides are also called *mustard oils*, because they all have a great resemblance to the essential oil of mustard, which consists of allyl sulphocarbimide $N\left\{\begin{matrix}C_3H_5\\CS\end{matrix}\right.$.

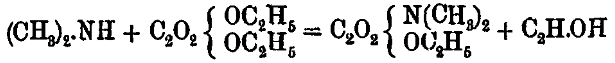
NITROGEN BASES OF METHYL.

When methyl iodide is heated in closed vessels with an alcoholic solution of ammonia, the hydriodides of the three amines, together with tetramethylammonium iodide, are formed at the same time. To separate these compounds the liquid is filtered, the greater part of the tetrammonium iodide, which is sparingly soluble in alcohol, being left behind. The filtrate is evaporated to dryness, and the residue distilled with caustic potash. The vapour is passed into a well-cooled receiver, in order to condense the dimethylamine and trimethylamine, whilst the greater part of the methylamine escapes and is absorbed by dilute hydrochloric acid. The mixture of the two bases, containing a little methylamine, is mixed with ethyl oxalate, when the following reactions take place:—

Methylamine forms methyloxamide :—

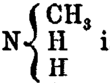
$$2(NH_2.CH_3) + C_2O_2(OC_2H_5)_2 = C_2O_2(NH.CH_3)_2 + 2(C_2H_5.OH)$$

Dimethylamine is converted into the ethyl ether of dimethyloxaminic acid :—

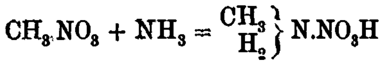


$$(CH_3)_2.NH + C_2O_2\left\{\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix}\right. = C_2O_2\left\{\begin{matrix}N(CH_3)_2\\OC_2H_5\end{matrix}\right. + C_2H.OH$$

Trimethylamine, which is not acted upon by the oxalic ether, is removed by distillation from a water bath, and the residue exhausted with water, which dissolves the dimethyl-oxamic ether, whilst methyloxamide is left behind.

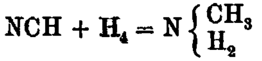


Methylamine $N\left\{\begin{matrix}CH_3\\H\\H\end{matrix}\right.$ is obtained by distilling the hydrochloride or methyloxamide with caustic potash. It is also formed by heating methyl nitrate with aqueous ammonia to 100° :—



$$CH_3.NO_3 + NH_3 = \left.\begin{matrix}CH_3\\H_2\end{matrix}\right\} N.NO_3H$$

On bringing hydrocyanic acid in contact with tin and hydrochloric acid it combines with the nascent hydrogen to form methylamine :—

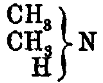


$$NCH + H_4 = N\left\{\begin{matrix}CH_3\\H_2\end{matrix}\right.$$

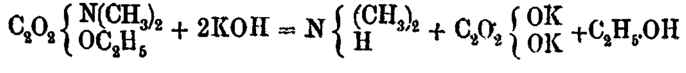
A fourth method to obtain this base is the decomposition of methyl carbimide by alkalis; this is the reaction by which it was discovered.

Methylamine is a colourless gas, condensible by means of a freezing mixture to a colourless, mobile liquid. It possesses a strong ammoniacal smell, and is more soluble in water than ammonia, one volume of water at the common temperature dissolving about 1,000 volumes of the gas. Methylamine is inflammable, and burns with a yellowish flame. The aqueous solution precipitates metallic salts like ammonia; the precipitate produced in copper salts is soluble in excess, forming a deep blue liquid, but the hydroxides of cobalt, nickel, and cadmium are insoluble in methylamine, whilst silver chloride is readily dissolved. With acids it forms neutral soluble salts; the platinum double chloride $(N(CH_3)_3HCl)_2 + PtCl_4$ crystallizes from boiling water in golden yellow plates.

Methylamine occurs in the brine of herrings and amongst the products of the destructive distillation of animal matter and wood.



Dimethylamine $\left.\begin{matrix}CH_3\\CH_3\\H\end{matrix}\right\} N$ is obtained by distilling ethyl dimethyloxamate with caustic potash :—



$$C_2O_2\left\{\begin{matrix}N(CH_3)_2\\OC_2H_5\end{matrix}\right. + 2KOH = N\left\{\begin{matrix}(CH_3)_2\\H\end{matrix}\right. + C_2O_2\left\{\begin{matrix}OK\\OK\end{matrix}\right. + C_2H_5.OH$$

It is a colourless gas possessing an ammoniacal smell, and condensing at + 8° to a mobile liquid.

Trimethylamine $\left.\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\right\}N$ boils at + 9·3°, possesses a strong smell of ammonia and herrings' brine, and is miscible with water. It occurs in many plants, as in the flowers of the hawthorn and the pear-tree, and in *Chenopodium vulvaria*, as well as in different animal liquids. Very often it is met with as a product of the decomposition of nitrogenous animal or vegetable compounds; thus herrings' brine contains it in so large a quantity that it can be easily prepared from it by distillation with alkalis.

When trimethylamine is mixed with methyl iodide, heat is evolved, *tetramethylammonium iodide* $N(CH_3)_4I$ being formed, a salt which forms colourless crystals and is not decomposed by alkalis. On treating its aqueous solution with freshly precipitated silver oxide, a strongly alkaline solution of the hydroxide $N(CH_3)_4OH$ is obtained, which by evaporation *in vacuo* over sulphuric acid is left behind as a crystalline mass, which is as caustic as caustic potash. When exposed to the air it rapidly absorbs water and carbon dioxide.

PHOSPHORUS BASES OF METHYL.

Methylphosphine $\left.\begin{matrix}CH_3\\H\\H\end{matrix}\right\}P$.—The hydriodide of this base is produced on heating a mixture of methyl iodide, phosphonium iodide, and zinc oxide in sealed tubes for four hours to 150°:—

$$2CH_3I + 2PH_4I + ZnO = 2(P(CH_3)H_2.HI) + ZnI_2 + H_2O$$

On adding water the hydriodide splits up into hydriodic acid and methylphosphine, a colourless gas, having a most penetrating and overpowering smell. By pressure or cold it is condensed to a light liquid, which boils at – 14°. On mixing the gas with air it takes oxygen up, forming white fumes, and when gently heated it takes fire. With acids it readily combines, forming well-defined salts, which are all decomposed by water. These salts possess the remarkable property of bleaching vegetable colours, whilst the free base does not act upon them. This can be easily shown by holding litmus paper, which has been partly moistened with an acid and partly with water, in the gaseous base, when only the portion moistened with the acid will be bleached. Amongst the salts the most characteristic is the hydriodide $N(CH_3)H_3I$, obtained in compact crystals by passing the gas into most concentrated hydriodic acid, whilst from hydriodic acid diluted with ether it crystallizes in iridescent plates.

On passing methylphosphine into fuming nitric acid it is oxidized dibasic methylphosphinic acid $PO_3(CH_3)H_2$ being formed, a white crystalline mass, readily soluble in water, and possessing an acid taste.

Dimethylphosphine $\left.\begin{matrix}CH_3\\CH_3\\H\end{matrix}\right\}P$.—The hydriodide of this base is formed together with methylphosphine, and remains behind after the addition of water in combination with zinc iodide:—

$$2CH_3I + PH_4I + ZnO = (CH_3)_2HP.HI, ZnI_2 + H_2O$$

This double compound is decomposed by caustic potash, and the free base obtained as a colourless liquid boiling at 25°. Exposed to the air it takes fire, and burns with a luminous phosphorus-like flame.

By the action of nitric acid it is converted into dimethylphosphinic acid $PO_2(CH_3)_2H$, which is monobasic and forms a white crystalline mass melting at 76° and volatilizing at a higher temperature without decomposition.

Trimethylphosphine $\left.\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\right\}P$ is formed by the action of zinc methyl upon phosphorus trichloride. It is a colourless liquid, boiling at 40° and possessing a peculiar penetrating smell. It combines with methyl iodide to form *tetramethylphosphonium iodide* $P(CH_3)_4I$, white crystals, the solution of which is decomposed by moist silver oxide with the formation of the strongly alkaline and caustic hydroxide $P(CH_3)_4OH$. The iodide is also formed together with trimethylphosphine hydriodide by heating methyl alcohol with phosphonium iodide in sealed tubes:—

$$3\left.\begin{matrix}CH_3\\H\end{matrix}\right\}O + PH_4I = (CH_3)_3P, HI + 3\left.\begin{matrix}H\\H\end{matrix}\right\}O$$

$$4\left.\begin{matrix}CH_3\\H\end{matrix}\right\}O + PH_4I = (CH_3)_4PI \quad + 4\left.\begin{matrix}H\\H\end{matrix}\right\}O$$

ARSENIC BASES OF METHYL.

The compounds of methyl with arsenic may be considered as being derived from arsenic trichloride:—

Arsenic Trichloride.

$$As\left\{\begin{matrix}Cl\\Cl\\Cl\end{matrix}\right.$$

Arsenmethyl Dichloride.

$$As\left\{\begin{matrix}CH_3\\Cl\\Cl\end{matrix}\right.$$

Arsendimethyl Chloride.

$$As\left\{\begin{matrix}CH_3\\CH_3\\Cl\end{matrix}\right.$$

Arsentrimethyl.

$$As\left\{\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\right.$$

These compounds combine (in a manner analogous to phosphorus trichloride) directly with one molecule of chlorine, and the compounds thus obtained are decomposed by heat with the elimination of methyl chloride:—

$$As(CH_3)_3Cl_2 = As(CH_3)_2Cl + CH_3Cl$$
$$As(CH_3)_2Cl_3 = As(CH_3)Cl_2 + CH_3Cl$$

The compound of arsenmethyl dichloride with chlorine can only exist at a very low temperature, as it is rapidly decomposed even below 0°:—

$$AsCH_3Cl_4 = AsCl_3 + CH_3Cl$$

Trimethylarsine $As(CH_3)_3$ is easily formed by the action of methyl iodide upon sodium arsenide $AsNa_3$. It is a colourless liquid, boiling at 120° and possessing an unbearable garlic-like odour. It combines readily with the iodides of the alcohol radicals.

Tetramethylarsonium Iodide $As(CH_3)_4I$ crystallizes in shining plates; its aqueous solution is easily acted upon by silver oxide. On evaporating the alkaline solution thus formed over sulphuric acid, the hydroxide $As(CH_3)_4OH$ is obtained in deliquescent crystals; it combines readily with acids, forming well-crystallized salts.

Compounds of Arsendimethyl.—The starting-point for the preparation of these compounds is the so-called *alcarsine* or *cacodyl oxide*, a highly poisonous liquid possessing a most horrible smell. This body is obtained on distilling a mixture of arsenic trioxide and potassium acetate, a mixture of *arsendimethyl oxide* with some *arsendimethyl* being thus formed, which owing to the presence of the latter compound, takes fire in the air. With fuming hydrochloric acid it yields *arsendimethyl chloride* $As(CH_3)_2Cl$, a colourless liquid boiling at 100°, and possessing a nauseous smell; its vapour attacks the eyes and the mucous membranes. By distilling the chloride with a solution of caustic potash it yields pure *arsendimethyl oxide* $\left.\begin{matrix}As(CH_3)_2\\As(CH_3)_2\end{matrix}\right\}O$, an oily liquid boiling at 120°, which is not spontaneously inflammable and does not fume when exposed to the air.

Arsendimethyl $\left.\begin{matrix}As(CH_3)_2\\As(CH_3)_2\end{matrix}\right\}$ *or Cacodyl* (*κακός, ὀδεῖν*), obtained by heating the chloride with zinc, is a heavy liquid, boiling at 170°. It possesses an arsenical penetrating smell, and is a very strong poison. In contact with the air it takes fire and burns with a yellow flame, giving off dense clouds of arsenic trioxide. When air is brought slowly in contact with it, it is oxidized to cacodyl oxide and cacodylic acid.

Cacodylic Acid $\left.\begin{matrix}As(CH_3)_2O\\H\end{matrix}\right\}O$ is best prepared by adding mercuric oxide to arsendimethyl oxide, which is covered by a layer of water: metallic mercury separates out, and on evaporating the solution, the acid is obtained in large colourless crystals, which are odourless and have a slightly acid taste. It is not poisonous.

Arsenmonomethyl Compounds.—Arsendimethyl trichloride yields, as we have seen, on heating, methyl chloride and arsenmonomethyl dichloride. The latter compound is also obtained by the action of dry hydrochloric acid upon cacodylic acid:—

$$\left.\begin{matrix}As(CH_3)_2O\\ H\end{matrix}\right\}O + 3HCl = As(CH_3)Cl_2 + CH_3Cl + 2H_2O$$

Arsenmonomethyl Chloride $AsCH_3Cl_2$ is a colourless strongly refracting liquid boiling at 135°; its vapours violently attack the mucous membranes. On adding water and potassium carbonate to it the oxide $AsCH_3O$ is obtained in colourless crystals, which smell like asafœtida. By the action of water and silver oxide upon the oxide or chloride the silver salt *arsenmonomethylic acid* $AsCH_3\left\{\begin{matrix}OAg\\ OAg\end{matrix}\right.$ is formed. The free acid, obtained by decomposing the barium salt with sulphuric acid, crystallizes in colourless plates and possesses a pure acid taste.

METHYLBORINE OR BORON-METHYL $B(CH_3)_3$

is formed by a singular reaction; it is obtained by acting on ethyl borate with zinc-methyl:—

$$2B\left\{\begin{matrix}OC_2H_5\\ OC_2H_5\\ OC_2H_5\end{matrix}\right. + 3Zn\left\{\begin{matrix}CH_3\\ CH_3\end{matrix}\right. = 2B\left\{\begin{matrix}CH_3\\ CH_3\\ CH_3\end{matrix}\right. + 3Zn\left\{\begin{matrix}OC_2H_5\\ OC_2H_5\end{matrix}\right.$$

It is a colourless gas, having a pungent smell; exposed to air it takes fire, burning with a smoky green flame. By strong pressure or cold it can be condensed to a liquid. It combines with dry ammonia, forming the compound $B(CH_3)_3NH_3$, a white crystalline mass.

COMPOUNDS OF METHYL WITH METALS.

Zinc Methide or Zinc-methyl $Zn(CH_3)_2$ is produced by heating zinc with methyl iodide. It is, however, much more readily formed when mercuric methide is heated with granulated zinc in a sealed tube for 24 hours to 120°. Zinc methide is a colourless mobile liquid, possessing a peculiar disagreeable smell. It takes fire in the air, burning with a greenish blue flame, and with the formation of dense clouds of zinc oxide. With water it forms zinc hydroxide and methane:—

$$Zn\left\{\begin{matrix}CH_3\\ CH_3\end{matrix}\right. + 2\left.\begin{matrix}H\\ H\end{matrix}\right\}O = Zn\left\{\begin{matrix}OH\\ OH\end{matrix}\right. + 2CH_4$$

On adding sodium to zinc methide, zinc separates out, and a crystalline compound $Zn(CH_3)_2 + NaCH_3$ is formed. It has not been possible so far to isolate from this compound pure *sodium methide* $NaCH_3$. On passing carbonic dioxide over it, it is absorbed, with evolution of heat and formation of sodium acetate:—

$$NaCH_3 + CO_2 = NaC_2H_3O_2$$

Mercuric Methide $Hg(CH_3)_2$.—Methyl iodide is not acted upon by liquid sodium amalgam, but on adding a small quantity of acetic ether, a brisk reaction set in, sodium iodide and mercury methide being formed. It is not understood what part the acetic ether plays in this reaction, as it remains unaltered.

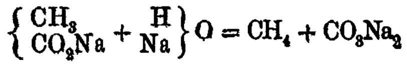
Mercuric methide is a heavy colourless liquid with a peculiar though not an unpleasant smell. It is most poisonous, is not acted upon by the air, and boils at 95°.

METHANE AND ITS SUBSTITUTION PRODUCTS.

Methane, Methyl Hydride, CH_4.—This gas occurs in nature, being always formed when vegetable matters decay in the absence of air. It is found in coal mines (firedamp), and in marshes and stagnant waters (marsh-gas), and in many districts it is evolved from the soil, as in Baku on the Caspian Sea, where the holy fires have been burning from time immemorial. Although the most simple of all hydrocarbons, it cannot be produced by direct combination of carbon and hydrogen, but is formed by passing hydrogen sulphide, mixed with the vapour of carbon disulphide, over red-hot copper:—

$$CS_2 + 2SH_2 + 4Cu_2 = CH_4 + 4Cu_2S$$

Pure methane is obtained by the action of water upon zinc methyl, but a readier method to prepare it is to heat a mixture of dry sodium acetate with twice its weight of soda lime:—



$$\left\{\begin{array}{l} CH_3 \\ CO_2Na \end{array}\right. + \left.\begin{array}{c} H \\ Na \end{array}\right\} O = CH_4 + CO_3Na_2$$

Methane is a colourless, inodorous gas, which burns with a pale flame. It has not yet been condensed to a liquid by the strongest pressure or cold. With ten volumes of air or with two volumes of oxygen it forms a mixture, which on applying a light ignites with a violent explosion. By exposing a mixture of equal volumes of marsh-gas and chlorine to direct sunlight an explosion takes place, with the separation of carbon; but in diffused light the action goes on more gently, the principal product being methyl chloride, and if an excess of chlorine is present higher chlorinated substitution products are formed. These bodies are generally regarded as compounds of dyad and triad radicals, but as they bear very little relation to other groups of carbon compounds they will be treated of here.

Methene Dichloride, Dichloromethane CH_2Cl_2 can be obtained by the action of chlorine upon marsh-gas, or by adding hydrochloric acid and zinc to an alcoholic solution of chloroform. It is a heavy liquid, smelling like chloroform and boiling at 41°.

Chloroform, Trichloromethane $CHCl_3$.—The third substitution product of marsh-gas is also formed by the action of bleaching powder on ethyl alcohol, and other carbon compounds. To prepare it ten parts of bleaching powder are mixed with forty parts of hot water in a large still, and one part of spirits of wine is added; a reaction soon sets in by which sufficient heat is evolved to drive the chloroform over.

Chloroform is a colourless mobile liquid, possessing a peculiar sweetish smell and taste. It boils at 62°, and has at 0° the specific gravity 1·525. The inhalation of its vapour produces anæsthesia, and it is therefore largely employed in surgical operations. It is also used as a solvent for iodine, bromine, alkaloids, gutta percha, &c.

The smallest quantity of chloroform can be easily detected by adding to the liquid to be tested a monamine (or aniline) and an alcoholic solution of caustic potash. When it is present in larger quantities the peculiar odour of the carbamines is given off at once, or after gently heating when only traces are present. *Vice versâ*, chloroform can be used for detecting the presence of a monamine.

Tetrachloromethane, Carbon Tetrachloride CCl_4 is best prepared by acting with chlorine upon chloroform in the sunlight; it may also be obtained by passing chlorine and carbon disulphide through a porcelain tube filled with fragments of porcelain. It is a heavy liquid, boiling at 77° and possessing the odour of chloroform. On heating it with an alcoholic solution of potash it yields potassium chloride, potassium carbonate, and water:—

$$CCl_4 + 6KOH = CO\left\{\begin{matrix}OK\\OK\end{matrix}\right. + 4KCl + 3H_2O$$

When its vapour mixed with hydrogen is passed through a glass-tube filled with broken glass, and heated to a dull red heat, hexachlorethane C_2Cl_6 is formed:—

$$2CCl_4 + H_2 = 2HCl + C_2Cl_6$$

Bromoform, Tribromomethane $CHBr_3$, a liquid resembling chloroform and boiling at 152°, is obtained by adding bromine to a solution of potash in ethyl alcohol; bromoform very often occurs in commercial bromine.

Tetrabromomethane, Carbon Tetrabromide CBr_4.—On heating bromine with carbon disulphide in sealed tubes to 180°, an exceedingly slow action sets in, which is very much accelerated by adding some iodine. To prepare tetrabromomsthane, two parts of carbon disulphide, fourteen parts of bromine, and three parts of iodine are heated to 150°

in sealed tubes for forty-eight hours. It is also readily formed by heating bromoform with bromine and iodine. Tetrabromomethane crystallizes in white shining plates, melting at 91°, and boiling with slight decomposition at 189·5°.

Iodoform, Tri-iodomethane CHI_3.—This compound is formed by acting with potash or potassium carbonate and iodine upon ethyl alcohol, aldehyde, acetone, and many other carbon compounds, but pure methyl alcohol yields no iodoform. It crystallizes in yellow scales, smells like saffron, melts at 120°, and is decomposed at a higher temperature, but may be volatilized in a current of steam. On heating it in a closed tube for some time to 150°, *methene di-iodide* or *di-iodomethane* CH_2I_2 is formed, a compound which can also be obtained by heating chloroform with fuming hydriodic acid :—

$$CHCl_3 + 4HI = CH_2I_2 + 3HCl + I_2$$

This compound is a yellowish heavy liquid, which boils at 181° and at − 2° solidifies to a crystalline mass.

Nitrochloroform, Nitrotrichloromethane, or Chloropicrin $C(NO_2)Cl_3$ is formed when methyl- or ethyl alcohol are distilled with salt, saltpetre, and sulphuric acid, and also by the distillation of many nitro-compounds with a solution of bleaching powder.

It is best prepared by mixing in a still, ten parts of bleaching powder with water to form a paste, and adding one part of picric acid $C_6H_2(NO_2)_3OH$; a violent reaction sets in and the chloropicrin distils over. It is a colourless liquid, possessing a most irritating smell, and boiling at 112°. On distilling it with acetic acid and iron-filings it is reduced to methylamine :—

$$C(NO_2)Cl_3 + 6H_2 = CH_3.NH_2 + 3HCl + 2H_2O$$

Nitroform, Trinitromethane, $CH(NO_2)_3$.—This body is produced by decomposing *trinitroacetonitrile* $C_2(NO_2)_3N$ (see Fulminates) with water :—

$$\left\{\begin{matrix} C(NO_2)_3 \\ CN \end{matrix}\right. + 2H_2O = CO_2 + NH_3 + CH(NO_2)_3$$

Nitroform is a weak acid ; the product of the reaction consists therefore of the ammonium salt. On acting on trinitroacetonitrile with caustic potash, the potassium salt $CK(NO_2)_3$ is obtained, which forms yellow crystals. On adding concentrated sulphuric acid to one of these salts, nitroform separates out as a light oily layer, which on cooling solidifies, forming colourless, cubical crystals. It has an unpleasant smell and bitter taste, and is highly inflammable. In water it dissolves with a yellow colour. On quickly heating it or one of its salts, it decomposes with a violent explosion.

Tetranitromethane $C(NO_2)_4$.—By passing a current of air through a solution of nitroform in a mixture of concentrated nitric and sulphuric acids, tetranitromethane distils over :—

$$CH(NO_2)_3 + \left.\begin{matrix}NO_2\\H\end{matrix}\right\}O = C(NO_2)_4 + \left.\begin{matrix}H\\H\end{matrix}\right\}O$$

It is a colourless mobile liquid, boiling at 126°, and solidifying at $-13°$. It is not explosive, and not inflammable, but on pouring it over red-hot charcoal a vivid combustion sets in.

Methine-trisulphonic Acid $CH\left\{\begin{matrix}SO_3H\\SO_3H\\SO_3H\end{matrix}\right.$—This acid is formed by heating calcium methyl-sulphate with a large excess of fuming sulphuric acid for some time to 100°. To obtain the free acid, the lead salt is decomposed by hydrogen sulphide; it crystallizes in long deliquescent needles. It is a powerful tribasic acid, decomposing nitrates and chlorides, and forming well-crystallized salts, of which the lead and barium salt are sparingly soluble in water.

Guanidine $C(NH)(NH_2)_2$.—This powerful base was first obtained from guanine $C_5H_5N_5O$, a compound occurring in guano. It is also formed by heating biuret (see page 67) in a current of dry hydrochloric acid gas.

Guanidine is also easily produced by heating cyanogen iodide with an alcoholic solution of ammonia:—

$$ICN + 2NH_3 = C(NH)\left\{\begin{matrix}NH_2\\NH_2\end{matrix}\right. + HI$$

or by the action of alcoholic ammonia upon chloropicrin:—

$$CCl_3NO_2 + 4NH_3 = C(NH)(NH_2)_2 + 3HCl + N_2 + 2H_2O$$

Guanidine combines with acids, forming crystalline salts, of which the nitrate is only sparingly soluble in water. When a solution of silver nitrate is added to its solution the compound $CH_5N_3.AgNO_3$ separates in colourless needles. On adding gold chloride to a moderately concentrated solution of guanidine hydrochloride the double salt $CH_5N_3\,ClH + AuCl_3$ crystallizes after some time in beautiful, deep-yellow, long needles.

To obtain the free base the hydrochloride or hydriodide is decomposed with a solution of silver sulphate, and baryta-water is added as long as a precipitate is formed. On evaporating the filtrate *in vacuo*, guanidine is left behind in colourless crystals, which are soluble in water and alcohol; it possesses a strongly alkaline taste, and readily absorbs carbon dioxide from the air.

FORMYL COMPOUNDS.

Methyl Aldehyde or *Formaldehyde* CH_2O is a colourless gas, possessing a pungent and suffocating smell. It is formed by passing a current of air charged with vapour of methyl alcohol over a coil of red-hot platinum wire. The product condensed in a well-cooled receiver consists of a solution of the aldehyde in methyl alcohol. Exposed to the air, it absorbs oxygen, the aldehyde being oxidized to formic acid. This oxidation takes place quickly on adding a little ammonia and silver nitrate to the liquid and heating the mixture gently; metallic silver separates out, which coats the sides of the vessel with a brilliant metallic mirror :—

$$CH_2O + Ag_2O = CH_2O_2 + Ag_2$$

Like other aldehydes, formaldehyde readily changes into a polymeric modification; for this reason it is impossible to isolate the pure compound from its solution, which, on evaporation *in vacuo* over sulphuric acid, leaves a white solid residue of *paraformaldehyde* $C_3H_6O_3$, a body which is also formed by heating dichloromethyl ether $\left.\begin{matrix} CH_2Cl \\ CH_2Cl \end{matrix}\right\} O$ with water, and further by the action of silver oxalate on methene iodide :—

$$3C_2O_4Ag_2 + 3CH_2I_2 = C_3H_6O_3 + 6AgI + 3CO + 3CO_2$$

Paraformaldehyde (formerly called *dioxymethene*) is a white indistinctly crystalline mass, which sublimes below 100° without previously melting. When it is heated in a closed vessel, it melts at 152°, and boils at a few degrees higher, at the same time being resolved into three molecules of gaseous formaldehyde. This gas can only be kept for a short time at the common temperature; when it is collected over mercury, the mercury soon begins to rise, the aldehyde being rapidly reconverted into the paraldehyde.

Formic Acid $\left.\begin{matrix} COH \\ H \end{matrix}\right\} O$.—This acid exists in the free state in stinging-nettles, in red ants, and in several species of caterpillars. It may be obtained by oxidizing methyl alcohol by means of dilute sulphuric acid and potassium chromate or manganese dioxide. Besides methyl alcohol a great number of other carbon compounds, such as sugar, gum, and starch, yield formic acid as a product of oxidation.

Formic acid is obtained synthetically by heating carbon oxide and caustic potash in closed vessels, to 100° :—

$$CO + \left.\begin{matrix} H \\ K \end{matrix}\right\} O = \left.\begin{matrix} COH \\ K \end{matrix}\right\} O$$

or by the action of moist carbon dioxide on potassium :—

$$2CO\left\{\begin{matrix} OH \\ OH \end{matrix}\right. + K_2 = CO\left\{\begin{matrix} OH \\ OK \end{matrix}\right. + \left.\begin{matrix} COH \\ K \end{matrix}\right\} O + \left.\begin{matrix} H \\ H \end{matrix}\right\} O$$

The best method, however, for preparing large quantities of formic acid consists in decomposing oxalic acid by heat in presence of glycerin :—

$$C_2H_2O_4 = CO_2 + CH_2O_2$$

The best yield is obtained by heating a mixture of anhydrous glycerin and crystallized oxalic acid $C_2H_2O_4 + 2H_2O$ from 90° to 100° as long as carbon dioxide is evolved; the residue is again heated with oxalic acid, and this process several times repeated. During the operation aqueous formic acid distils over; at first a dilute acid, which after each addition of oxalic acid becomes more concentrated, until, according to the equation—

$$C_2H_2O_4 + 2H_2O = CO_2 + CH_2O_2 + 2H_2O$$

from each 126 parts of oxalic acid, 82 parts of aqueous formic acid, containing 56 per cent. of real acid, have been formed.

To prepare anhydrous formic acid, the hot aqueous acid is neutralized with litharge or white lead; on cooling, lead formate crystallizes out, which after having been well dried is placed in a retort, and dry hydrogen sulphide passed over it, at the same time applying a gentle heat. The distillate is freed from an excess of hydrogen sulphide by rectifying it over a little lead formate.

Pure formic acid is a colourless liquid, solidifying at + 1° in shining plates, and boiling at 100°. It possesses a sour and pungent odour, and a very acid taste, and is so corrosive that it produces blisters on the skin.

The salts of formic acid or *formates* are for the most part soluble in water, and crystallize well. When calcium formate is subjected to fractional distillation different products are formed, amongst which formaldehyde is found:—

$$\left.\begin{matrix} CHO_2 \\ CHO_2 \end{matrix}\right\} Ca = CH_2O + CaCO_3$$

On heating the sodium salt, hydrogen is given off and sodium oxalate is formed:—

$$\begin{matrix} HCO.ONa \\ \\ HCO.ONa \end{matrix} = 2H + \begin{matrix} CO.ONa \\ | \\ CO.ONa \end{matrix}$$

Ammonium Formate $\left.\begin{matrix} COH \\ NH_4 \end{matrix}\right\} O$ is obtained by bringing together dry ammonia and anhydrous formic acid. On rapidly heating it, it decomposes into water and hydrocyanic acid:—

$$\left.\begin{matrix} COH \\ NH_4 \end{matrix}\right\} O = 2H_2O + HCN$$

It has already been mentioned that by the inverse reaction hydrocyanic acid takes up water and yields ammonium formate. Hydrocyanic acid is therefore the *nitrile* of formic acid, or it stands in the same relation to formic acid as acetonitrile (methyl cyanide) to acetic acid.

The most characteristic of the salts of formic acid is *lead formate*

$(CHO_2)_2Pb$, crystallizing from a hot aqueous solution in white, shining, rhombic prisms, which are only sparingly soluble in cold water.

Silver Formate CHO_2Ag is a white precipitate, which on exposure to the light rapidly blackens. When heated with water it is decomposed, metallic silver separating out, whilst carbon dioxide escapes:—

$$2\left.\begin{matrix}\mathrm{COH}\\\mathrm{Ag}\end{matrix}\right\}\mathrm{O} = \left.\begin{matrix}\mathrm{COH}\\\mathrm{H}\end{matrix}\right\}\mathrm{O} + \mathrm{CO_2} + \mathrm{Ag_2}$$

When aqueous formic acid is gently heated with mercuric oxide, carbon dioxide is given off, and mercurous formate crystallizes out in white shining scales:—

$$3\left.\begin{matrix}\mathrm{COH}\\\mathrm{H}\end{matrix}\right\}\mathrm{O} + 2\mathrm{HgO} = \left.\begin{matrix}\mathrm{(COH)_2}\\\mathrm{Hg_2}\end{matrix}\right\}\mathrm{O_2} + \mathrm{CO_2} + 2\mathrm{H_2O}$$

On boiling this salt with water, a decomposition analogous to that of the silver salt ensues, metallic mercury and carbon dioxide being formed. These reactions of the silver and mercury salts are made use of as a means for detecting formic acid.

Methyl Formate $\left.\begin{matrix}\mathrm{COH}\\\mathrm{CH_3}\end{matrix}\right\}\mathrm{O}$ is obtained by distilling methyl sulphate with sodium formate:—

$$2\left.\begin{matrix}\mathrm{COH}\\\mathrm{Na}\end{matrix}\right\}\mathrm{O} + \left.\begin{matrix}\mathrm{CH_3}\\\mathrm{CH_3}\end{matrix}\right\}\mathrm{SO_4} = 2\left.\begin{matrix}\mathrm{COH}\\\mathrm{CH_3}\end{matrix}\right\}\mathrm{O} + \left.\begin{matrix}\mathrm{Na}\\\mathrm{Na}\end{matrix}\right\}\mathrm{SO_4}$$

It is a colourless liquid, having a pleasant smell, and boiling at 33°·4. Chlorine acts on it slowly in the sunlight, *perchloromethyl formate* $\left.\begin{matrix}\mathrm{COCl}\\\mathrm{CCl_3}\end{matrix}\right\}\mathrm{O}$ being formed, a colourless liquid, possessing a very pungent smell, and boiling at about 180°. When its vapour is passed through a glass tube heated to 350°, it is transformed into carbonyl dichloride:—

$$\left.\begin{matrix}\mathrm{COCl}\\\mathrm{CCl_3}\end{matrix}\right\}\mathrm{O} = 2\mathrm{COCl_2}$$

Methyl Chloroformate or Methyl Chlorocarbonate $\left.\begin{matrix}\mathrm{COCl}\\\mathrm{CH_3}\end{matrix}\right\}\mathrm{O}$, a heavy colourless liquid, possessing a suffocating smell, and boiling at 75°, is formed by the action of carbonyl dichloride upon anhydrous methyl alcohol.

Formamide $COH.NH_2$.—This compound, standing intermediate between ammonium formate and hydrocyanic acid, is obtained by heating ammonium formate to 140° in the presence of urea, which is transformed into ammonium carbonate by the water given off.

Formamide can also be obtained by saturating ethyl formate with dry ammonia, and heating the mixture in sealed glass tubes for two days in a water-bath:—

$$\left.\begin{matrix}\mathrm{COH}\\\mathrm{C_2H_5}\end{matrix}\right\}\mathrm{O} + \mathrm{NH_3} = \mathrm{COH.NH_2} + \mathrm{C_2H_5.OH}$$

It is a colourless liquid which boils at about 194°, at the same time being partially decomposed into ammonia and carbon monoxide, and partially into hydrocyanic acid and water. By treating it with a cold solution of caustic potash, ammonia and potassium formate are produced.

ETHYL COMPOUNDS.

ETHYL ALCOHOL $C_2H_5.OH$.

This compound is manufactured on the large scale, and is the most important body of the whole group, being the starting-point for the preparation of all the other ethyl compounds, which have been most fully investigated. Ethyl alcohol or spirits of wine is obtained by the vinous fermentation of sugar, a decomposition taking place in dilute solutions of sugar in the presence of yeast, and by which the greatest portion of the sugar is resolved into carbon dioxide and ethyl alcohol:—

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

Besides these two products other compounds are also formed in smaller quantities, such as glycerin, succinic acid, &c. A more complete account of this decomposition will be found under the head of Fermentation.

Fermented liquors are prepared from the juice of grapes, apples, beet-roots, and from corn and potatoes, the two latter being first treated with an infusion of malt, to convert the starch which they contain into sugar (*vide* Sugar).

The fermented liquid is first distilled to separate the dilute aqueous spirit from the non-volatile substances, and then rectified in stills which have an arrangement by which the more volatile alcohol distils whilst the greater portion of the water remains behind. The spirit thus obtained contains besides water also fusel-oil (which consists of higher members of the alcohol series), and which is removed by treating the raw spirit with freshly heated charcoal.

Although the boiling-point of water is much higher than that of alcohol, the latter cannot be completely separated by distillation; the strongest spirit thus obtained containing still about ten per cent. of water.

To obtain pure anhydrous ethyl alcohol, or *absolute alcohol*, a retort is filled with fragments of freshly burnt quicklime, and the strongest spirit poured on to it. After standing for a day, it is distilled with the aid of a water-bath; the distillate is nearly anhydrous; to remove the last traces of water it is necessary to leave it for some time in contact with caustic baryta, and to rectify it again.

Perfectly pure ethyl alcohol is a colourless mobile liquid, which is almost odourless; it boils at 78°·4, and when it is cooled down to

– 100° it becomes viscid, but does not solidify. Its specific gravity at 0° is 0·80625, and at 15° 0·79367. Ethyl alcohol is very inflammable, and burns with a blue, non-luminous flame. It absorbs moisture with great avidity, and is miscible with water in all proportions, the mixture evolving heat and undergoing contraction. The greatest contraction takes place when forty-six parts by weight of alcohol or one molecule are mixed with fifty-four parts or three molecules of water.

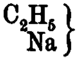
Alcohol is a solvent for resins, fats, essential oils, and many other bodies which are insoluble in water. Many salts and also gases dissolve in it too, some of them being even more soluble in it than in water.

As the value of spirits of wine depends on the quantity of alcohol contained in it, it is of great importance to have a rapid and exact method for ascertaining its strength. When the spirit only contains water, the amount of alcohol is easily obtained by ascertaining the specific gravity of the liquid by means of a delicate hydrometer, and subsequent reference to accurate tables, showing the percentage of alcohol. When the liquid to be tested contains sugar or other non-volatile substances, as those found in wine and beer, one-third of a measured quantity of the liquid is distilled off, all the alcohol coming over with the first portion. The distillate is then diluted with water up to the original volume, and examined with the hydrometer. In these determinations the temperature must be observed, and corrections for deviations be made, when the temperature differs from that at which the instrument has been graduated, from the fact that alcohol expands considerably with an increase of temperature.

The "proof spirit" of the excise contains 50·8 per cent. by weight of alcohol, and has at 15°·5 (60° F.) the specific gravity 0·920. Owing to the high duty on pure spirit the Government allow the sale of a mixture of ninety parts of strong spirit, and ten parts of crude wood spirit, called "methylated spirit," for manufacturing and scientific purposes.

The quantities of alcohol in different spirituous liquors vary very much. Brandy, whisky, &c., contain 40—50 per cent.; wines from 17 per cent. (Madeira, port) to 7—8 per cent. (light claret and hock); whilst ale and porter contain 6—8 per cent., and German beer about 4 per cent.

The least trace of alcohol in an aqueous solution can be readily detected by adding to the liquid a little benzoyl chloride, which is only slowly acted upon by water, but forms with alcohol at once ethyl benzoate, a liquid having a very characteristic aromatic odour, and which will be readily perceived after the excess of the chloride has been destroyed by caustic potash. By means of this reaction the presence of 0·1 per cent. of alcohol in a few cb.cm. of water can be shown.

Sodium Ethylate  $\left.\begin{matrix}C_2H_5\\Na\end{matrix}\right\}O$.—Sodium dissolves in absolute alcohol with the evolution of hydrogen; on cooling colourless crystals separate, consisting of a compound of sodium ethylate with alcohol, the latter acting like water of crystallization. On heating these crystals in a current of pure, dry hydrogen to 180°—200°, all the alcohol is expelled and pure sodium ethylate is left behind, a white, light, porous mass, which is decomposed by water into caustic soda and alcohol. Potassium ethylate is a similar compound.

Ethyl Chloride C_2H_5Cl is a colourless gas, possessing a pleasant ethereal odour; on cooling it condenses to a liquid, which boils at 12°·5. It is inflammable, and burns with a smoky green-bordered flame. To prepare it, absolute alcohol is saturated with dry hydrochloric acid gas, and the liquid, after standing for a few days, is heated. The vapour is washed with warm water, dried over fused calcium chloride, and condensed in a receiver, surrounded by a freezing mixture. Ethyl chloride is formed in large quantities as a bye-product in the manufacture of chloral hydrate (*vide* Chloral).

Ethyl Bromide C_2H_5Br is best prepared by adding gradually six parts of bromine to a well-cooled mixture of six parts of spirits of wine and one part of amorphous phosphorus. After standing for some time the bromide is distilled off, the distillate washed with caustic soda solution, dried over calcium chloride, and rectified. Ethyl bromide is a colourless heavy liquid, possessing a sweet ethereal odour and boiling at 39°.

Ethyl Iodide C_2H_5I.—To obtain this compound one part of amorphous phosphorus and five parts of alcohol are placed into a retort, and ten parts of powdered iodine are gradually added, and the mixture allowed to stand over night. The iodide is distilled off next day and purified like the bromide. The formation of ethyl iodide takes place according to the equation :—

$$5(C_2H_5.OH) + 5I + P = 5C_2H_5I + PO_4H_3 + H_2O$$

It is a colourless heavy liquid, having a peculiar, somewhat garlic-like odour, and boiling at 72°. When it is exposed to the light and air it assumes a brown colour, iodine being set free. Ethyl iodide is very largely used for the preparation of other ethyl compounds, as it very readily exchanges its iodine by double decomposition. It is prepared on the large scale, and used in the manufacture of the violets known as Hofmann's.

Ethyl Oxide, Diethyl Ether $\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O$.—This body, commonly called "ether,"[1] can be formed by several reactions, the most simple being the action of ethyl iodide upon sodium ethylate:—

$$\left.\begin{matrix}C_2H_5\\Na\end{matrix}\right\}O + \left.\begin{matrix}I\\C_2H_5\end{matrix}\right\} = \left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O + \left.\begin{matrix}I\\Na\end{matrix}\right\}$$

Ether is manufactured on the large scale by heating a mixture of strong alcohol and concentrated sulphuric acid to 140°. The reaction takes place in two stages; in the first ethylsulphuric acid and water are formed:—

---

[1] The name of the radical *ethyl* is derived from ether; the affix "yl," which has been introduced for the purpose of designating organic radicals, being derived from ὕλη "the matter or stuff of which a substance is made."

$$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O + \left.\begin{matrix}H\\H\end{matrix}\right\}SO_4 = \left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}SO_4 + \left.\begin{matrix}H\\H\end{matrix}\right\}O$$

The ethylsulphuric acid acts at 140° upon another molecule of alcohol; hydrogen and ethyl change places, and ether and sulphuric acid are formed:—

$$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}SO_4 + \left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O = \left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O + \left.\begin{matrix}H\\H\end{matrix}\right\}SO_4$$

The ether and the water produced distil off, whilst the sulphuric acid remains behind, ready to convert another quantity of alcohol into ether. This method is called the process of "continuous etherification," as a current of alcohol may be passed without interruption through the acid heated up to 140°, and thus large quantities be converted into ether by means of a small quantity of sulphuric acid. The reason why we are unable to transform, as the theory indicates, an unlimited quantity of alcohol into ether with a given quantity of sulphuric acid, is that, besides the chief reaction, secondary reactions take place at the same time, by which more water is formed than is removed by the distillation, and the acid becoming too weak the formation of ethylsulphuric acid at last ceases.

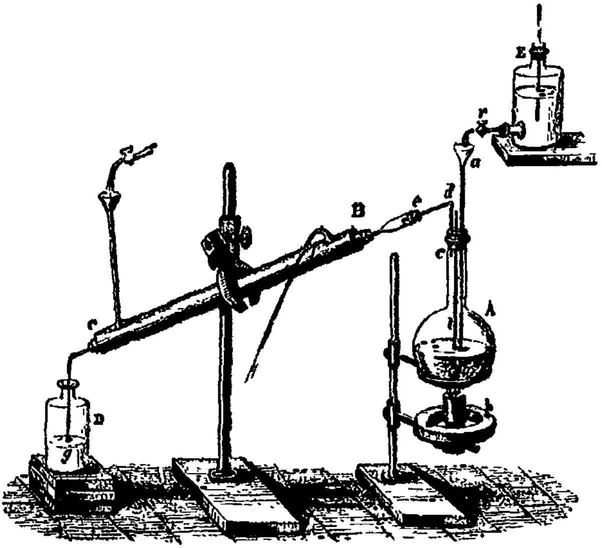


FIG. 9.

To illustrate in the lecture room the preparation of ether by this process, the apparatus (Fig. 9) is used.

The crude ether thus obtained swims as a light layer upon the water, and generally contains besides alcohol also sulphuric dioxide. To obtain it in a pure state it is washed with dilute soda solution, dried over quicklime, and rectified with the aid of a water-bath. To obtain it completely free from water and alcohol, it must be left in contact with metallic sodium so long as any action takes place, and then be distilled off.

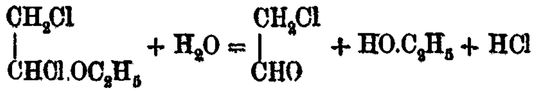
Pure ethyl ether is a very mobile liquid, possessing a characteristic penetrating odour and a burning taste. It boils at 34°·5, and has at 0° the specific gravity 0·736. It is somewhat soluble in water, and mixes with alcohol in all proportions. It is highly inflammable, burning with a luminous flame. Its vapour, which is 2·557 times heavier than water, and which can be poured from vessel to vessel like carbon dioxide, forms with air an explosive mixture; great care must therefore be taken, in working with large quantities of such a volatile and inflammable body, to avoid the presence of any light.

Methyl-ethyl Ether $\left.\begin{matrix}CH_3\\C_2H_5\end{matrix}\right\}O$ is obtained by the action of ethyl iodide upon sodium methylate, and may also be prepared by heating methyl sulphuric acid with ethyl alcohol. It is a very volatile liquid, boiling at 12°.

On acting upon well-cooled ether with chlorine in the diffused daylight, substitution products are formed.

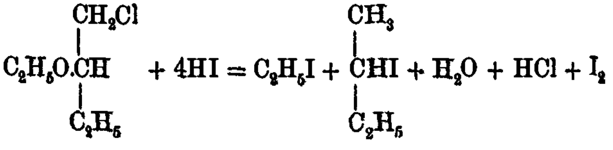
Monochlorethyl Oxide $\left.\begin{matrix}C_2H_4Cl\\C_2H_5\end{matrix}\right\}O$ is a limpid liquid boiling at 97°.

Dichlorethyl Oxide $\left.\begin{matrix}C_2H_3Cl_2\\C_2H_5\end{matrix}\right\}O$ boils at 140°, and possesses a pungent smell; when heated with water in sealed tubes to 120°, it yields ethyl alcohol and monochloracetaldehyde :—



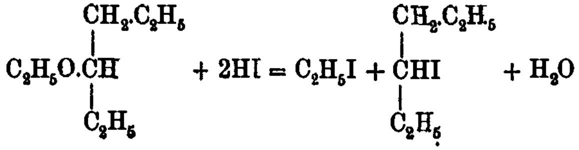
$$\begin{matrix}CH_2Cl\\|\\CHCl.OC_2H_5\end{matrix} + H_2O = \begin{matrix}CH_2Cl\\|\\CHO\end{matrix} + HO.C_2H_5 + HCl$$

By the action of zinc ethide on dichlorethyl oxide, the compounds $\left.\begin{matrix}C_2H_3Cl(C_2H_5)\\C_2H_5\end{matrix}\right\}O$ and $\left.\begin{matrix}C_2H_3(C_2H_5)_2\\C_2H_5\end{matrix}\right\}O$ are produced. When the first of these is heated with fuming hydriodic acid, it is decomposed with the formation of ethyl iodide and secondary butyl iodide :—



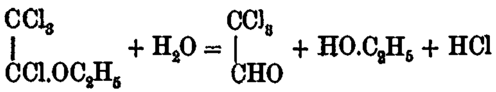
$$\begin{matrix}CH_2Cl\\|\\C_2H_5O.CH\\|\\C_2H_5\end{matrix} + 4HI = C_2H_5I + \begin{matrix}CH_3\\|\\CHI\\|\\C_2H_5\end{matrix} + H_2O + HCl + I_2$$

Diethylated ethyl oxide is converted by hydriodic acid into ethyl iodide and a secondary hexyl iodide:—



$$\begin{array}{c} CH_2.C_2H_5 \\ | \\ C_2H_5O.CH \\ | \\ C_2H_5 \end{array} + 2HI = C_2H_5I + \begin{array}{c} CH_2.C_2H_5 \\ | \\ CHI \\ | \\ C_2H_5 \end{array} + H_2O$$

Tetrachlorethyl Oxide $\left.\begin{matrix} C_2HCl_4 \\ C_2H_5 \end{matrix}\right\} O$ is a liquid boiling at 189°, and smelling like fennel. On heating it with water to 100° it yields alcohol and trichloracetaldehyde (chloral):—



$$\begin{array}{l} CCl_3 \\ | \\ CCl.OC_2H_5 \end{array} + H_2O = \begin{array}{l} CCl_3 \\ | \\ CHO \end{array} + HO.C_2H_5 + HCl$$

Perchlorethyl Oxide $\left.\begin{matrix} C_2Cl_5 \\ C_2Cl_5 \end{matrix}\right\} O$ is the final product obtained by acting with chlorine on tetrachlorethyl oxide in the sunlight. It forms white crystals melting at 69°, and decomposing at 300° into hexachlorethane and triacetyl chloride:—

$$\left.\begin{matrix} C_2Cl_5 \\ C_2Cl_5 \end{matrix}\right\} O = C_2Cl_6 + C_2Cl_3OCl$$

Ethyl Nitrate $\left.\begin{matrix} C_2H_5 \\ NO_2 \end{matrix}\right\} O$ may be obtained by gradually adding perfectly pure concentrated nitric acid to absolute alcohol, which is contained in a vessel surrounded by ice. Common nitric acid exerts a violent action on alcohol, oxidation takes place, and nitric trioxide is given off, which acts on a portion of the alcohol, forming ethyl nitrite; but if a substance is present which is capable of destroying any nitrogen trioxide as soon as it is formed, ethyl nitrate will be produced. This compound can easily be prepared in quantities by mixing one part of urea with five parts of pure nitric acid and three parts of commercial absolute alcohol, and distilling the mixture. To the residue the same quantities of acid and alcohol may be added, and the operation be repeated so long as no red fumes appear.

Ethyl nitrate is a liquid possessing a fragrant odour and boiling at 86°. It burns with a bright white flame, and its vapour, when heated above the boiling-point, decomposes with a violent explosion.

Ethyl Nitrite $C_2H_5.NO_2$ is a mobile, very volatile liquid, having a very agreeable odour of apples, and boiling at 16·5°. It is best prepared by acting upon potassium nitrite with a cold mixture of alcohol and sulphuric acid. Caustic potash decomposes it into alcohol, and potassium nitrite and nascent hydrogen acts on it in the following way:—

$$C_2H_5NO_2 + 3H_2 = C_2H_5.OH + H_2O + NH_3$$

The *sweet spirit of nitre* of pharmacy, which is prepared by distilling a mixture of alcohol, sulphuric and nitric acid with copper wire, consists chiefly of a solution of ethyl nitrite in spirits of wine, but contains also aldehyde and other products.

Nitro-ethane $C_2H_5.NO_2$.—This isomeride of ethyl nitrite is produced by heating ethyl iodide with silver nitrite. It is a limpid and very refractive liquid, boiling at 112°, and possessing a peculiar pleasant smell. It has acid properties; with alcoholic soda it solidifies to a white magma, which after expelling the alcohol has the composition $C_2H_4Na.NO_2$. On heating this compound it explodes like gun-cotton. By the action of nascent hydrogen it is converted into ethylamine:—

$$C_2H_5.NO_2 + 3H_2 = C_2H_5.NH_2 + 2H_2O$$

This reaction shows that in this compound the nitrogen is combined with carbon, whilst in ethyl nitrite the nitrogen is linked to the ethyl by means of an atom of oxygen, the constitution of the isomerides being:—

Ethyl Nitrite.

$$C_2H_5\,O.NO$$

Nitro-ethane.

$$C_2H_5.N\left\{\begin{matrix}O\\O\end{matrix}\right.$$

Ethyl Perchlorate $C_2H_5.ClO_4$.—This is the only ether of the oxyacids of chlorine known. It is obtained by distilling small quantities of an intimate mixture of potassium perchlorate and potassium ethylsulphate, as a colourless liquid having an agreeable smell; the dry compound explodes most violently by the faintest concussion.

Ethyl Hydrosulphate or Ethylsulphuric Acid $\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}SO_4$.—This compound, also called *sulphovinic acid*, is formed by mixing sulphuric acid with alcohol. The yield varies according to the strength of the alcohol and the heat evolved on mixing it with the acid. By heating the mixture and allowing it to stand for some time, more will be formed, but it is not possible to convert all the alcohol or all the sulphuric acid present into ethylsulphuric acid. The liquid is diluted with a large quantity of water, neutralized in the cold with barium carbonate or lead oxide, and the filtrate evaporated to a small bulk on a water-bath, and left to crystallize. From the solution of the barium or lead salt the free acid is obtained by dilute sulphuric acid and evaporating the filtrate in a vacuum. It forms a strongly acid, syrupy liquid, which is very easily decomposed, and has not yet been obtained quite free from sulphuric acid. Ethylsulphuric acid is monobasic, and forms well-crystallized salts, which are all soluble in water; on heating them with water they decompose, alcohol and a sulphate being formed.

Ethyl Sulphate $\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}SO_4$ is not formed, like methyl sulphate, by the action of ethylsulphuric acid upon ethyl alcohol, but is obtained by passing the vapour of sulphur trioxide into well-cooled anhydrous ether, a reaction perfectly analogous to the formation of sulphuric acid from the trioxide and water:—

$$\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O + SO_3 \quad = \quad \left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}SO_4$$

The product of the reaction, when shaken with four volumes of water and one of ether, separates into two layers, the lower consisting of an aqueous solution of ethylsulphuric acid and other products, whilst the upper layer consists of an ethereal solution of ethyl sulphate. By heating it gently the ether is volatilized, and ethyl sulphate remains as a syrupy liquid, smelling like peppermint. It cannot be distilled, as it is decomposed by heat. Ethyl sulphate is also produced by the action of sulphuryl chlorhydrate on absolute alcohol:—

$$2\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O + \left.\begin{matrix}HO\\Cl\end{matrix}\right\}SO_2 = \left.\begin{matrix}C_2H_5O\\C_2H_5O\end{matrix}\right\}SO_2 + HCl + H_2O$$

Ethyl Sulphite $\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}SO_3$ is obtained by acting on alcohol with thionyl chloride $SOCl_2$ (the chloride of sulphurous acid):—

$$SOCl_2 + 2C_2H_5.OH = \left.\begin{matrix}C_2H_5O\\C_2H_5O\end{matrix}\right\}SO + 2HCl$$

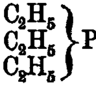
and is also formed, together with other products, by adding absolute alcohol to chlorine bisulphide S_2Cl_2. It is a limpid liquid, boiling at 160°, and smelling like peppermint; it is slowly decomposed by water, and quickly when heated with a solution of caustic potash. By acting on it with caustic potash in the cold, *potassium ethylsulphite* $\left.\begin{matrix}K\\C_2H_5\end{matrix}\right\}SO_3$ is formed, which crystallizes in silky scales. The free ethylsulphurous acid is not known, but an isomeric compound called *ethylsulphonic acid* exists, which is formed by oxidizing ethyl sulphide, hydrosulphide, and other sulphur compounds of ethyl. The potassium salt of this acid is also obtained by heating ethyl iodide with a concentrated solution of potassium sulphite. The free ethylsulphonic acid is best prepared by decomposing the lead salt with hydrogen sulphide. On evaporating the solution it is left as a heavy oil, which after some time solidifies to a crystalline mass. It is a monobasic acid and a very stable compound; its salts crystallize well.

The existence of these isomeric compounds shows that the two hydrogen atoms of sulphurous acid have not the same value, or occupy different positions in the molecule, the constitution of these different compounds being probably as follows:—

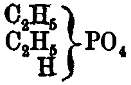
Sulphurous Acid.	Ethyl Sulphite.
H—O—S—O—O—H	C_2H_5—O—S—O—O—C_2H_5

Potassium Ethylsulphite.	Ethylsulphonic Acid.
K—O—S—O—O—C_2H_5	C_2H_5—O—S—O—O—H

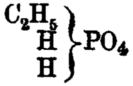
Ethyl Phosphates.—Orthophosphoric acid forms three ethyl compounds:—

Triethyl Phosphate 

$$\left.\begin{matrix}C_2H_5\\C_2H_5\\C_2H_5\end{matrix}\right\}PO_4$$

Diethylphosphoric Acid 

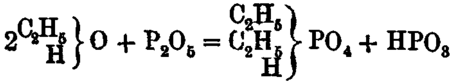
$$\left.\begin{matrix}C_2H_5\\C_2H_5\\H\end{matrix}\right\}PO_4$$

Ethylphosphoric Acid 

$$\left.\begin{matrix}C_2H_5\\H\\H\end{matrix}\right\}PO_4$$

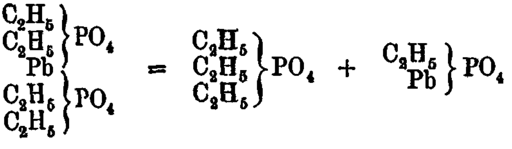
Triethyl Phosphate is obtained by heating silver phosphate with ethyl iodide, or by acting with phosphorus oxychloride upon sodium ethylate. It is a colourless liquid, boiling at 215°, and having a peculiar smell. It is soluble in water, by which it is slowly decomposed.

Diethylphosphoric Acid is a monobasic acid, which is only known in solution. It is formed by bringing alcohol vapour gradually in contact with phosphorus pentoxide:—



$$2\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O + P_2O_5 = \left.\begin{matrix}C_2H_5\\C_2H_5\\H\end{matrix}\right\}PO_4 + HPO_3$$

Lead diethylphosphate is soluble in water and crystallizes in needles. When heated it melts, and at a higher temperature it is decomposed into triethyl phosphate and lead ethylphosphate:—



$$\left.\begin{matrix}\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}PO_4\\Pb\\\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}PO_4\end{matrix}\right. = \left.\begin{matrix}C_2H_5\\C_2H_5\\C_2H_5\end{matrix}\right\}PO_4 + \left.\begin{matrix}C_2H_5\\Pb\end{matrix}\right\}PO_4$$

Ethylphosphoric Acid is also formed by heating alcohol with syrupy phosphoric acid. It is a colourless, syrupy liquid, of a very sour taste. The lead salt is almost insoluble in water; the barium salt is readily soluble, and crystallizes in brilliant hexagonal prisms.

Ethyl Pyrophosphate $P_2O_7(C_2H_5)_4$, obtained by the action of ethyl iodide on silver pyrophosphate, is a viscid liquid.

Ethyl Phosphites.—By acting with phosphorus trichloride on absolute alcohol or sodium ethylate, triethyl phosphite $PO_3(C_2H_5)_3$ is formed, a liquid boiling at 191° and possessing a disagreeable odour. By avoiding an excess of alcohol the first product of the reaction consists of $P(OC_2H_5)Cl_2$, a limpid liquid boiling at 117°; water decomposes it with the formation of alcohol, phosphorous acid, and hydrochloric acid.

Ethylphosphorous Acid $\left.\begin{matrix}C_2H_5\\H_2\end{matrix}\right\}PO_3$.—This monobasic acid is pro-

I 2

duced by the action of aqueous alcohol on phosphorus trichloride. Its barium salt is deliquescent; the lead salt crystallizes from a hot aqueous solution in white scales.

Ethyl Arsenate $\left.\begin{matrix}C_2H_5\\C_2H_5\\C_2H_5\end{matrix}\right\}AsO_4$, a colourless liquid, is produced by the action of silver arsenate upon ethyl iodide. It boils at 235° with slight decomposition, and in contact with water it is resolved into ethyl alcohol and arsenic acid.

Ethyl Arsenite $\left.\begin{matrix}C_2H_5\\C_2H_5\\C_2H_5\end{matrix}\right\}AsO_3$ is prepared from ethyl iodide and silver arsenite. It is a colourless liquid, boiling at 166°: water decomposes it into alcohol and arsenic trioxide.

Ethyl Borate $\left.\begin{matrix}C_2H_5\\C_2H_5\\C_2H_5\end{matrix}\right\}BoO_3$ is formed by the action of boron trichloride upon alcohol, and by heating boron trioxide with alcohol, or by distilling a mixture of anhydrous borax with potassium ethylsulphate. It is a mobile liquid possessing a peculiar smell and bitter taste, and boiling at 119°. It is decomposed by water; its alcoholic solution burns with a green flame, giving off white clouds of boric acid.

Ethyl Silicates.—When absolute alcohol is added to silicon tetrachloride as long as hydrochloric acid is given off, and the mixture subjected to distillation, first normal *ethyl silicate* $Si(OC_2H_5)_4$ passes over, a colourless liquid, having a pleasant ethereal odour, boiling at 162°, and burning with a brilliant white flame, emitting a dense white smoke of finely divided silica. After the normal silicic ether has distilled over, the temperature rises and *diethyl silicate* $SiO(OC_2H_5)_2$ distils, a colourless liquid, boiling at 350°. Both compounds are slowly decomposed by water, and when in contact with moist air they become gradually thicker and thicker, until at last silicic acid is left behind in the form of a perfectly transparent, hard mass.

By the action of silicon tetrachloride upon silicic ether the volatile compounds $\left.\begin{matrix}(C_2H_5O)_3\\Cl\end{matrix}\right\}Si$, $\left.\begin{matrix}(C_2H_5O)_2\\Cl_2\end{matrix}\right\}Si$, and $\left.\begin{matrix}C_2H_5O\\Cl_3\end{matrix}\right\}Si$ are formed By acting on these compounds with different alcohols, a great number of silicic ethers, containing two or more alcohol radicals, can be obtained.

Ethyl Carbonate $\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}CO_3$ is a limpid liquid, having a pleasant smell and boiling at 126°. It is obtained by the action of silver carbonate upon ethyl iodide.

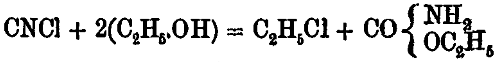
When carbon dioxide is passed into an alcoholic solution of potassium ethylate, a white compound, consisting of *potassium ethylcarbonate* $\left.\begin{matrix}K\\C_2H_5\end{matrix}\right\}CO_3$ separates out, which is decomposed by water with the formation of alcohol and acid potassium carbonate; the free *ethylcarbonic acid* is not known.

Ethyl Orthocarbonate $C(OC_2H_5)_4$.—This compound, corresponding to the normal ethyl silicate, is formed by acting with sodium upon a solution of chloropicrin in absolute alcohol:—

$$4C_2H_5ONa + CCl_3NO_2 = C(OC_2H_5)_4 + 3NaCl + NaNO_2$$

It is a colourless liquid, boiling at 158° and having an aromatic smell. When heated with alcoholic potash it is decomposed, potassium carbonate, ether, and alcohol being formed.

Ethyl Carbamate $CO\left\{\begin{matrix}NH_2\\OC_2H_5\end{matrix}\right.$.—This compound is formed when dry ammonia acts upon ethyl carbonate at the common temperature, whilst if the two substances are heated together to 100°, carbamide is produced. Ethyl carbamate, also called *urethane*, is a colourless crystalline solid, melting and boiling without decomposition at 180°; it is also obtained when cyanogen chloride is passed into alcohol:—

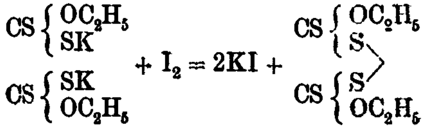


$$CNCl + 2(C_2H_5.OH) = C_2H_5Cl + CO\left\{\begin{matrix}NH_2\\OC_2H_5\end{matrix}\right.$$

Ethyl Sulphocarbonate $\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}CS_3$ is a yellow oil, boiling at 240°, which is produced by acting with sodium sulphocarbonate upon an alcoholic solution of ethyl iodide. Nitric acid oxidizes it to ethylsulphonic acid.

Xanthic Acid or Ethyldisulphocarbonic Acid $\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}COS_2$.—The potassium salt of this acid separates in white silky needles when carbon disulphide is added to a hot alcoholic solution of potash. By adding cold dilute sulphuric acid to this salt, xanthic acid is obtained as a colourless oil, having a penetrating smell. It is a very unstable compound, being resolved at about 25° into carbon disulphide and alcohol. The xanthates of the metals of the alkalis and alkaline earths are soluble in water, and precipitated by most metallic salts. *Lead xanthate* $(C_2H_5.COS_2)_2Pb$ is a white precipitate, crystallizing from hot alcohol in needles. The copper salt is a beautiful yellow powder.

When iodine is added to an alcoholic solution of a xanthate, the following reaction takes place:—



$$\begin{matrix}CS\left\{\begin{matrix}OC_2H_5\\SK\end{matrix}\right.\\CS\left\{\begin{matrix}SK\\OC_2H_5\end{matrix}\right.\end{matrix} + I_2 = 2KI + \begin{matrix}CS\left\{\begin{matrix}OC_2H_5\\S\diagdown\end{matrix}\right.\\ \qquad\rangle\\CS\left\{\begin{matrix}S\diagup\\OC_2H_5\end{matrix}\right.\end{matrix}$$

Ethyldisulphocarbonyl disulphide is formed, crystallizing in brilliant white prisms, melting at 28°, and possessing a peculiar but not unpleasant odour.

Ethyl Xanthate $CS\left\{\begin{matrix}SC_2H_5\\OC_2H_5\end{matrix}\right.$ is produced when ethyl chloride and potassium xanthate are left together in an alcoholic solution for some time. It is a colourless liquid of high refractive power, boiling at 200°, and possessing a powerful alliaceous odour.

Ethyl Chloroformate or Ethyl Chlorocarbonate $CO\left\{\begin{matrix}Cl\\OC_2H_5\end{matrix}\right.$, a colourless liquid, possessing a suffocating smell, is produced by the action of carbonyl chloride on alcohol. On mixing it with an alcoholic solution of sodium sulphide, *ethyl dicarbothionate* $S\left\{\begin{matrix}CO.OC_2H_5\\CO.OC_2H_5\end{matrix}\right.$ is produced, a colourless oil with a peculiar odour, and boiling at 180°. By treating it with caustic potash potassium carbonate and ethyl sulphide are formed. Neither the free dicarbothionic acid $S\left\{\begin{matrix}CO.OH\\CO.OH\end{matrix}\right.$ nor any of its metallic salts have been obtained.

Ethyl Formate, Formic Ether $\left.\begin{matrix}COH\\C_2H_5\end{matrix}\right\}O$ is prepared by distilling a mixture of alcohol and sulphuric acid with sodium formate. A cheaper method consists in heating glycerin, oxalic acid, and alcohol together in a flask, which is connected with a reversed condenser. Formic acid is formed, which in the nascent state acts upon the alcohol, ethyl formate and water being produced. Formic ether boils at 55°, and possesses a fragrant smell like peaches; it is used for the preparation of artificial rum and arrack.

When sodium is added to a mixture of chloroform and alcohol, the so-called *tribasic formic ether* or *ethyl orthoformate* $CH(OC_2H_5)_3$ is obtained:—

$$CHCl_3 + 3C_2H_5.ONa = 3ClNa + CH(OC_2H_5)_3$$

This ether is a colourless liquid, possessing a pleasant smell, and boiling at 146°. On heating it with acetic acid it yields ethyl formate and ethyl acetate:—

$$CH(OC_2H_5)_3 + 2\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O = \left.\begin{matrix}COH\\C_2H_5\end{matrix}\right\}O + 2\left.\begin{matrix}C_2H_3O\\C_2H_5\end{matrix}\right\}O + H_2O$$

CYANOGEN COMPOUNDS OF ETHYL.

Ethyl Cyanide or Ethyl Carbamine $CN.C_2H_5$ is formed by heating ethyl iodide with silver cyanide, but is best prepared by adding an alcoholic solution of chloroform and ethylamine to powdered caustic potash; a violent reaction ensues, and the cyanide distils over:—

$$CHCl_3 + C_2H_5.NH_2 = 3HCl + C_2H_5.NC$$

It is a colourless liquid, boiling at 77°, and possessing, like all carbamines, a most penetrating and overpowering smell; it is poisonous. With dry hydrochloric acid it combines with a violent reaction; to obtain the pure compound both substances must be mixed in an ethereal solution at a very low temperature. A crystalline body is obtained, having a sour and bitter taste; it dissolves in water with decomposition, ethylamine and formic acid being formed. The same decomposition occurs by the action of dilute acids on ethyl carbamine:—

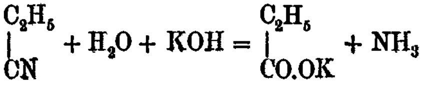
$$C_2H_5.NC + 2H_2O = C_2H_5.NH_2 + CH_2O_2$$

On heating the carbamine with a concentrated solution of potash a complicated reaction sets in, and amongst other products *ethylformamide* $N\left\{\begin{matrix}COH\\C_2H_5\\H\end{matrix}\right.$ is obtained, a liquid having a sweet taste, and boiling at 200°.

Propionitrile $C_2H_5.CN$ is the chief product obtained on distilling a mixture of potassium cyanide and potassium ethylsulphate. The distillate must be treated with a dilute acid in order to remove small quantities of the isomeric carbamine. Propionitrile boils at 97°, and possesses a penetrating but not unpleasant smell. It combines with acids; thus with anhydrous hydrobromic acid it forms the compound $C_3H_5N.2HBr$, which is decomposed by water with the formation of propionic acid:—

$$C_3H_5N + 2HBr + 2H_2O = C_3H_6O_2 + NH_4Br + HBr$$

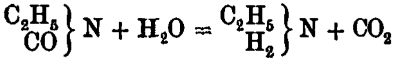
A similar reaction takes place on boiling the nitrile with a solution of caustic potash:—



$$\begin{matrix}C_2H_5\\|\\CN\end{matrix} + H_2O + KOH = \begin{matrix}C_2H_5\\|\\CO.OK\end{matrix} + NH_3$$

Ethyl Cyanate, Cyanetholine $\left.\begin{matrix}CN\\C_2H_5\end{matrix}\right\}O$ is a thick non-volatile liquid, insoluble in water, which is formed when cyanogen chloride acts upon sodium ethylate. It absorbs hydrochloric acid and is converted into a white crystalline mass, which on heating gives off ethyl chloride, whilst cyanuric acid remains behind.

Ethyl Carbimide $\left.\begin{matrix}CO\\C_2H_5\end{matrix}\right\}N$, a compound isomeric with ethyl cyanate, is obtained by distilling a mixture of potassium cyanate and potassium ethylsulphate. It appears most likely that in this reaction first ethyl cyanate is formed, which, however, at the high temperature undergoes a molecular change, being converted into the carbimide. This body, prior to the discovery of the real cyanate, was believed to be the latter compound, and is still called cyanic ether. It is a colourless liquid, boiling at 60°, and possessing a pungent smell, irritating the eyes. With hydrochloric acid it forms a liquid compound boiling at 95°, which by water is decomposed into carbon dioxide and ethylamine. The same products are formed when the carbimide is boiled with caustic potash:—



$$\left.\begin{matrix}C_2H_5\\CO\end{matrix}\right\}N + H_2O = \left.\begin{matrix}C_2H_5\\H_2\end{matrix}\right\}N + CO_2$$

When gaseous cyanic acid is passed into absolute alcohol, so much heat is evolved that the liquid begins to boil. On cooling, colourless shining prisms of *ethyl allophanate* $C_2H_3N_2O_3.C_2H_5$ crystallize out. By the action of caustic baryta on this ether the barium salt of *allophanic acid* $C_2H_4N_2O_3$ is obtained, but from this salt the free acid cannot be isolated, nor indeed are other salts known. A series of allophanic ethers, however, has been prepared by acting with cyanic acid on different alcohols.

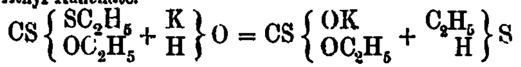
When barium allophanate is treated with a dilute acid, carbon dioxide is given off and urea is formed. This decomposition explains the constitution of allophanic acid, which stands to biuret in the same relation as carbamic acid to urea:—

Biuret. Allophanic Acid.

$$NH\left\{\begin{matrix}CO.NH_2\\CO.NH_2\end{matrix}\right. \qquad NH\left\{\begin{matrix}CO.NH_2\\CO.OH\end{matrix}\right.$$

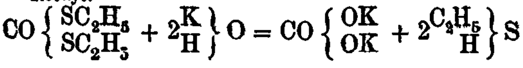
Ethyl Sulphocyanate $\left.\begin{matrix}C_2H_5\\CN\end{matrix}\right\}S$, a colourless oily liquid, boiling at 146°, and possessing a smell like leek, is formed by distilling a mixture of potassium sulphocyanate and potassium ethylsulphate. When this ether is heated with sulphuric acid, a copious evolution of carbon dioxide takes place, and a colourless volatile liquid, having a strong alliaceous smell, is formed, which has the composition and the same boiling-point as ethyl xanthate. These bodies are, however, not identical, for whilst the latter compound is decomposed by an alcoholic solution of potash into potassium ethyl sulphocarbonate and ethyl hydrosulphide, the isomeric compound, which has been called *carbonyl-disulpho-diethyl*, yields by the same treatment potassium carbonate and ethyl hydrosulphide. The cause of this isomerism is explained by the following equations:—

Ethyl Xanthate.



$$CS\left\{\begin{matrix}SC_2H_5\\OC_2H_5\end{matrix}\right. + \left.\begin{matrix}K\\H\end{matrix}\right\}O = CS\left\{\begin{matrix}OK\\OC_2H_5\end{matrix}\right. + \left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}S$$

Carbonyl-disulpho-diethyl.



$$CO\left\{\begin{matrix}SC_2H_5\\SC_2H_5\end{matrix}\right. + 2\left.\begin{matrix}K\\H\end{matrix}\right\}O = CO\left\{\begin{matrix}OK\\OK\end{matrix}\right. + 2\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}S$$

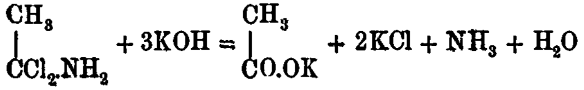
Ethylsulphocarbimide or Ethyl Mustard-oil $N\left\{\begin{matrix}CS\\C_2H_5\end{matrix}\right.$, which is isomeric with ethyl sulphocyanate, is prepared from ethylamine in exactly the same way as the methyl compound is obtained from methylamine. It is a colourless liquid, possessing a pungent smell and irritating the eyes; in contact with the skin it produces reddening, and a burning pain.

ETHYLAMINES.

The different amines of ethyl are prepared from ethyl chloride or iodide in the same way as the methylamines are obtained from methyl iodide. To obtain them on the small scale ethyl iodide is heated with alcohol and strong aqueous ammonia in sealed glass tubes to 100°. To prepare large quantities of them it is best to use the crude ethyl chloride, which is obtained as a bye-product in the manufacture of chloral hydrate, and which is heated in large iron digesters with alcoholic ammonia. After the reaction is finished the liquid is separated by filtration from the ammonium chloride, and the alcohol distilled off. The residue, after drying on a water-bath, is decomposed by a concentrated solution of caustic soda, and the light layer consisting of the three bases treated with oxalic ether in exactly the same way as the amines of methyl, for although the boiling-points of the ethyl bases differ very much, it is singular that it is not possible to separate them by fractional distillation.

Ethylamine $\left.\begin{array}{c}C_2H_5\\H\\H\end{array}\right\}N$ is a very mobile liquid, smelling like ammonia, and boiling at 18·7°. It is miscible with water, and is a stronger base than ammonia, from which it differs in its reactions chiefly by redissolving precipitated aluminium hydroxide, when added in excess. The hydrochloride or ethylammonium chloride $N(C_2H_5)H_3Cl$ crystallizes in thin plates; it is a deliquescent salt, and soluble in absolute alcohol. The sulphate does not crystallize, and is very soluble in water and alcohol.

When chlorine is passed into an aqueous solution of ethylamine, *dichlorethylamine* $C_2H_3Cl_2.NH_2$ separates as a yellow heavy oil, having a very penetrating smell and boiling at 91°. By alkalis it is decomposed with the formation of acetic acid:—



$$\begin{array}{l}CH_3\\|\\CCl_2.NH_2\end{array} + 3KOH = \begin{array}{l}CH_3\\|\\CO.OK\end{array} + 2KCl + NH_3 + H_2O$$

On passing dry carbon dioxide into ethylamine, ethylammonium carbamate $CO\left\{\begin{array}{l}NH.C_2H_5\\O.N(C_2H_5)H_3\end{array}\right.$ is formed, a white solid, corresponding to ammonium carbamate (*vide* page 65).

Ethylamine has also been obtained by several other reactions. It was discovered by the action of caustic potash on ethyl carbimide, and is produced by heating ethyl nitrate with ammonia, and by acting with nascent hydrogen upon acetonitrile. It occurs also amongst the volatile bases formed by the destructive distillation of bones and other animal substances.

Diethylamine $\left.\begin{matrix} C_2H_5 \\ C_2H_5 \\ H \end{matrix}\right\} N$ is a liquid boiling at 57°, and possessing an ammoniacal smell; it is soluble in water. On distilling its hydrochloride with a concentrated solution of potassium nitrate *nitrosodiethyline* $\left.\begin{matrix} (C_2H_5)_2 \\ NO \end{matrix}\right\} N$ is formed, a liquid boiling at 177°, and which by the action of aqueous hydrochloric acid is again converted into diethylamine.

Triethylamine $\left.\begin{matrix} C_2H_5 \\ C_2H_5 \\ C_2H_5 \end{matrix}\right\} N$ is a light colourless liquid, strongly alkaline, and only sparingly soluble in water, boiling at 89°. On heating its hydrochloride with potassium nitrite, ethyl alcohol and nitrosodiethyline are formed.

Triethylamine combines readily with ethyl iodide, heat being evolved during the reaction, and *tetrethylammonium iodide* $N(C_2H_5)_4I$ is formed, a salt which is soluble in water and forms large colourless crystals. On treating its solution with freshly precipitated silver oxide, the hydroxide $N(C_2H_5)_4OH$ is obtained, which has a bitter and very caustic taste. On evaporating its solution *in vacuo* it is left as a crystalline, deliquescent mass. Like caustic potash it attacks and dissolves the skin, saponifies fats, and precipitates metallic salts, but does not redissolve chromic hydroxide. On heating the hydroxide it is resolved into water, ethene, and triethylamine.

With acids it forms soluble salts, which crystallize well. On adding platinum chloride to a solution of tetrethylammonium chloride, $2[N(C_2H_5)_4Cl] + PtCl_4$ is obtained as a yellow, crystalline precipitate.

ETHYLATED UREAS.

Compound ureas, or carbamide in which hydrogen is replaced by alcohol radicals, can be obtained in a manner similar to that in which common urea is produced from ammonia and cyanic acid, viz. either by acting with cyanic acid upon an amine or by treating a carbimide with ammonia or an amine.

Ethyl-carbamide $CO\left\{\begin{matrix} NH.C_2H_5 \\ NH_2 \end{matrix}\right.$.—This compound is obtained by the action of ammonia upon ethyl carbimide, as well as by combining cyanic acid with ethylamine. It crystallizes from water in long colourless prisms, and combines with acids like common urea; its nitrate is readily soluble in water.

Diethyl-carbamide exists in two metameric modifications; one having the constitution $CO\left\{\begin{matrix}NH.C_2H_5\\NH.C_2H_5\end{matrix}\right.$ is produced by acting with ethylamine upon ethyl carbimide. It crystallizes in long prisms, fuses at 107°, boils at 263° and yields on boiling with potash solution, potassium carbonate and ethylamine.

Its isomeride $CO\left\{\begin{matrix}NH_2\\N(C_2H_5)_2\end{matrix}\right.$ is formed by treating diethylamine with cyanic acid. It is decomposed by caustic potash with the formation of potassium carbonate, ammonia, and diethylamine.

Triethyl-carbamide $CO\left\{\begin{matrix}NH.C_2H_5\\N(C_2H_5)_2\end{matrix}\right.$, a crystalline solid, soluble in water, fusing at 63° and boiling at 223°, has been prepared from diethylamine and ethyl carbimide.

Ureas containing more than three alcohol radicals have not yet been obtained, as triamines do not act either upon carbimides or on cyanic acid.

Ethylated Sulphocarbamides have been produced by analogous reactions from the so-called mustard oils. Thus ammonia and ethyl sulphocarbimide form *ethyl-sulphocarbamide* $CS\left\{\begin{matrix}NH_2\\NH.C_2H_5\end{matrix}\right.$, white crystals, which melt at 106°. By acting with ethylamine on the same mustard-oil, we obtain *diethyl-sulphocarbamide* $CS\left\{\begin{matrix}NH.C_2H_5\\NH.C_2H_5\end{matrix}\right.$, a white, crystalline solid. When its aqueous solution is boiled with mercuric oxide, oxygen is exchanged for sulphur, and diethyl-carbamide and mercuric sulphide are formed. On heating its alcoholic solution with ethylamine and mercuric oxide, a strongly alkaline solution is obtained, *triethyl-guanidine* being formed:—

$$C\left\{\begin{matrix}NH.C_2H_5\\S\\NH.C_2H_5\end{matrix}\right. + N.C_2H_5.H_2 + HgO = C\left\{\begin{matrix}NH.C_2H_5\\N.C_2H_5\\NH.C_2H_5\end{matrix}\right. + H_2O + HgS$$

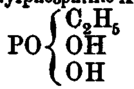
This compound is as powerful a base as common guanidine; its solution rapidly absorbs carbon dioxide from the air, and is converted into a crystalline mass.

PHOSPHORUS BASES OF ETHYL.

Ethylphosphine $\left\{\begin{matrix}C_2H_5\\H\\H\end{matrix}\right.$.—The hydriodide of this base is obtained from ethyl iodide, phosphonium iodide, and zinc oxide, in the same way as the corresponding compound in the methyl series. The base, set free by means of water, is a colourless liquid having a strong refractive power, lighter than water, boiling at 25°, and without any action on vegetable colours. Its odour is most overpowering, resembling that of the carbamines, and producing an intensely bitter taste in the mouth and deep down in the throat. In contact with chlorine, bromine, or fuming nitric acid it takes fire. Its vapour bleaches cork like chlorine, and india-rubber in contact with it becomes transparent and brittle. It combines with sulphur and carbon disulphide, forming liquid compounds, and with concentrated hydrochloric, hydrobromic, and hydriodic acid it forms crystalline salts. The hydrochloride gives with platinum chloride the double salt $[P(C_2H_5)H_3Cl]_2 + PtCl_4$, crystallizing in splendid crimson needles. The hydriodide forms large, four-sided, thin, iridescent plates.

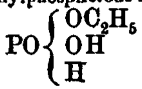
Nitric acid acts on the base in a similar way as on the methyl base, *ethylphosphinic acid* $PO_3(C_2H_5)H_2$ being formed, a crystalline solid, which melts at 44°, and at a higher temperature volatilizes without decomposition. This compound is isomeric with ethylphosphorous acid, from which it differs by being a bibasic acid whilst the latter is monobasic; the constitution of the two acids being represented by the following formulæ:—

Ethylphosphinic Acid.



$$PO\begin{cases} C_2H_5 \\ OH \\ OH \end{cases}$$

Ethylphosphorous Acid.



$$PO\begin{cases} OC_2H_5 \\ OH \\ H \end{cases}$$

Diethylphosphine $P\begin{cases} C_2H_5 \\ C_2H_5 \\ H \end{cases}$ is formed together with ethylphosphine, and isolated in the same way as the dimethyl-compound. It is a colourless, light, refractive liquid, boiling at 85°, and having a neutral reaction. The odour is penetrating and very persistent, but quite different from that of ethylphosphine. It absorbs oxygen rapidly, with much evolution of heat, the liquid sometimes taking fire. With sulphur and carbon disulphide it forms liquid compounds, and with acids salts, which, with the exception of the hydriodide, do not crystallize well.

Diethylphosphinic Acid $PO_3(C_2H_5)_2H$ is a liquid, and forms crystalline salts.

Triethylphosphine $P\begin{cases} C_2H_5 \\ C_2H_5 \\ C_2H_5 \end{cases}$.—The hydriodide of this base is produced by heating absolute alcohol with phosphonium iodide in sealed tubes for some hours to 160°:—

$$3(C_2H_5.OH) + PH_4I = (C_2H_5)_3PHI + 3H_2O$$

Triethylphosphine is also formed by the action of zinc ethide upon phosphorus trichloride. Phosphorus trichloride is added drop by drop to a solution of zinc-ethyl in ether, contained in a flask filled with carbon dioxide; a violent reaction sets in, zinc chloride and triethylphosphine being formed, which are separated by adding solid caustic potash and water, by which sufficient heat is evolved to volatilize the base.

It is a colourless, refractive liquid, lighter than water, and boiling at 127·5°. Its odour in the concentrated state is most powerful and unpleasant, but when diluted it becomes fragrant, and resembles very much that of hyacinths. When it comes in contact with the air it absorbs oxygen and is converted into *triethylphosphine oxide* $PO(C_2H_5)_3$, white needle-shaped crystals, boiling at 240°. When this oxidation goes on very rapidly, so much heat is evolved that the liquid takes fire. Triethylphosphine is only a weak base, and forms salts which do not crystallize well; the hydrochloride combines with platinum chloride forming $[P(C_2H_5)_3HCl]_2 + PtCl_4$, a crystalline precipitate.

Triethylphosphine also combines with sulphur, forming *triethylphosphine sulphide* $PS(C_2H_5)_3$, which crystallizes from water in long needles, melting at 94°. The most characteristic property of this base is, however, that with carbon disulphide it forms the compound $P(C_2H_5)_3CS_2$, which is insoluble in water and crystallizes in beautiful red needles. This reaction is made use of to detect traces of carbon disulphide, as in coal gas.

Iodide of ethyl and triethylphosphine combine readily, with evolution of much heat, to *tetrethylphosphonium iodide*, separating from water in fine crystals. It has also been obtained by heating absolute alcohol and phosphonium iodide:—

$$4(C_2H_5.OH) + PH_4I = P(C_2H_5)_4I + 4H_2O$$

This salt, which is not decomposed by alkalis, yields with silver oxide and water the hydroxide $P(C_2H_5)_4OH$, a white crystalline and very alkaline mass, which readily absorbs carbon dioxide from the air, and yields with acids soluble and crystalline salts. On heating the hydroxide, ethane is evolved and triethylphosphine oxide is left behind.

ARSENIC BASES OF ETHYL.

Sodium arsenide $AsNa_3$ is violently attacked by ethyl iodide, *arsendiethyl* $As_2(C_2H_5)_4$ and *triethylarsine* $As(C_2H_5)_3$ being formed, which can be separated by distilling the product in an apparatus filled with carbon dioxide; *triethylarsine*, being the more volatile compound, distilling first. It is a colourless liquid, which refracts light strongly and boils with partial decomposition at 140°. It possesses a most disagreeable odour; when exposed to the air it absorbs oxygen, emitting white fumes without taking fire; the oxide $AsO(C_2H_5)_3$, an oily liquid, being formed. On heating triethylarsine with sulphur, the sulphide $AsS(C_2H_5)$ is obtained, which crystallizes in large prisms. Triethylarsine also readily combines with ethyl iodide to form *tetrethylarsonium iodide* $As(C_2H_5)_4I$, a salt which with moist silver oxide yields the hydroxide, a colourless, deliquescent mass, and a very powerful base.

Arsendiethyl or Ethyl-cacodyl $\left\{\begin{matrix}As(C_2H_5)_2\\As(C_2H_5)_2\end{matrix}\right.$ is a yellowish liquid possessing a most intolerable smell, boiling at about 190°, and taking fire in the air. It combines directly with sulphur and with the elements of the chlorine group. By admitting air gradually to an alcoholic solution, *ethyl-cacodylic acid* $\left.\begin{matrix}As(C_2H_5)_2O\\H\end{matrix}\right\}O$ is formed, crystallizing in deliquescent plates. It has a sour taste and forms crystalline salts, which are soluble in water.

Arsenmonethyl compounds have not yet been obtained.

ANTIMONY BASES OF ETHYL.

Triethylstibine or Stibethyl $Sb\left\{\begin{matrix}C_2H_5\\C_2H_5\\C_2H_5\end{matrix}\right.$ is obtained by heating ethyl iodide with an alloy of potassium and antimony (SbK_3) in an atmosphere of carbon dioxide. It is a heavy, mobile, colourless liquid, boiling at 158°, and possessing a powerful odour resembling that of onions. Exposed to the air it takes fire, but when it is slowly oxidized in an alcoholic solution, *stibethyl oxide* $Sb(C_2H_5)_3O$ is obtained, a viscid mass, readily soluble in water and combining with acids. On adding hydrochloric acid to its solution, *stibethyl chloride* $Sb(C_2H_5)_3Cl_2$ is precipitated, a colourless liquid, which smells like turpentine, and is also formed by the direct union of stibethyl and chlorine.

Tetrethylstibonium Iodide $Sb(C_2H_5)_4I$ forms larger transparent crystals; it is readily acted upon by silver oxide and water; the hydroxide thus formed is a thick, strongly alkaline liquid.

BISMUTH BASES OF ETHYL.

Triethylbismuthine $Bi\left\{\begin{matrix}C_2H_5\\C_2H_5\\C_2H_5\end{matrix}\right.$ is obtained by the action of ethyl iodide upon an alloy of bismuth and potassium; it is a heavy colourless liquid, possessing a disagreeable smell, and resembling triethylstibine in most of its properties, its compounds, however, being less stable than those of the latter. On adding mercuric chloride to its solution *mercuric chlorethide* $Hg\left\{\begin{matrix}C_2H_5\\Cl\end{matrix}\right.$ is precipitated, and the solution contains *bismuthethyl dichloride* $Bi(C_2H_5)Cl_2$, which on evaporation is obtained in small crystals.

BORETHYL OR TRIETHYLBORINE $Bo\left\{\begin{matrix}C_2H_5\\C_2H_5\\C_2H_5\end{matrix}\right.$

This compound is prepared by gradually adding ethyl borate to zinc-ethyl:—

$$2Bo(OC_2H_5)_3 + 3Zn\,(C_2H_5)_2 = 2Bo(C_2H_5)_3 + 3Zn(OC_2H_5)_2$$

Triethylborine is a colourless liquid, boiling at 95°, and possessing an irritating odour; its vapour strongly attacks the mucous membranes and eyes. In contact with air it takes fire, burning with a smoky green flame; but when air is only very gradually brought in contact with it, the compound $Bo\left\{\begin{matrix}C_2H_5\\OC_2H_5\\OC_2H_5\end{matrix}\right.$ is formed, a liquid boiling at 125°, and which is decomposed by water into alcohol and $Bo(OH)_2C_2H_5$, a crystalline solid, having a sweet taste. On heating triethylborine with concentrated hydrochloric acid, ethane is evolved, and bor-diethyl chloride $BoCl(C_2H_5)_2$ left behind.

COMPOUNDS OF ETHYL AND SULPHUR.

Ethyl Hydrosulphide, or Mercaptan $\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}S$ is formed by the action of ethyl chloride, iodide, or potassium ethylsulphate upon potassium hydrosulphide. To prepare it a solution of caustic potash is saturated with hydrogen sulphide and then distilled with a concentrated solution of potassium ethylsulphate. It may also be obtained by the action of phosphorus pentasulphide upon alcohol:—

$$P_2S_5 + 5\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O = P_2O_5 + 5\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}S$$

Mercaptan is a colourless liquid, having a nauseous, intolerable smell, like onions, and boiling at 36°. It is almost insoluble in water and very inflammable, burning with a blue flame. On evaporating it by a rapid current of air, so much heat is absorbed that a portion of the liquid solidifies into a crystalline mass. The alkaline metals dissolve in it with evolution of hydrogen and formation of *mercaptides* as $\left.\begin{matrix}C_2H_5\\K\end{matrix}\right\}S$. Other metals also are capable of replacing hydrogen in mercaptan, this compound having the character of a weak acid like hydrogen sulphide. By adding mercuric oxide to mercaptan a violent reaction ensues, water and *mercuric mercaptide* $Hg(SC_2H_5)_2$ being formed (*mercurio aptum*). This compound is insoluble in water; from an alcoholic solution it crystallizes in white, silky scales; it is readily decomposed by dry hydrogen sulphide, the products being mercuric sulphide and mercaptan, which by this method is readily obtained in a perfectly pure state.

Ethyl Sulphide $\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}S$.—To prepare this compound ethyl chloride is passed into a boiling alcoholic solution of potassium sulphide. It is a mobile, colourless liquid, boiling at 91°, and possessing a nauseous smell like mercaptan. Dilute nitric acid oxidizes it, *ethyl sulphoxide* $(C_2H_5)_2SO$, an oily, non-volatile liquid, being formed. By fuming nitric acid it is transformed into *diethylsulphane* $(C_2H_5)_2SO_2$, which forms colourless crystals, fusing at 70° and boiling at 248°. By adding zinc and hydrochloric acid to its aqueous solution it is reduced to ethyl sulphide, and on boiling it for some time with nitric acid it is oxidized to ethylsulphonic acid.

Ethyl sulphide readily combines with ethyl iodide, forming *triethylsulphine iodide* $S(C_2H_5)_3I$, a crystalline compound soluble in water, and which by the action of water and silver oxide is converted into *triethylsulphine hydroxide* $S(C_2H_5)_3OH$, a powerful base, forming deliquescent crystals and combining with acids, yielding well-defined salts.

Ethyl Disulphide $\left.\begin{matrix}C_2H_5S\\C_2H_5S\end{matrix}\right\}$, a colourless liquid, boiling at 151°, and having a very disagreeable smell, is formed by distilling a mixture of potassium disulphide and potassium ethylsulphate, or by acting with iodine upon sodium mercaptide:—

$$2C_2H_5SNa + I_2 = 2NaI + \left.\begin{matrix}C_2H_5S\\C_2H_5S\end{matrix}\right\}$$

COMPOUNDS OF ETHYL WITH SELENIUM AND TELLURIUM.

These compounds are formed by reactions quite analogous to those by which the sulphides of ethyl are obtained, the corresponding metallic selenides and tellurides being employed in place of metallic sulphides.

Ethyl Hydroselenide, or Selenium Mercaptan $\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}Se$ is a liquid possessing a most intolerable smell, and forming with mercuric oxide a crystalline mercaptide.

Ethyl Selenide $\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}Se$ is a yellow liquid with a most disagreeable smell, which is oxidized by nitric acid to *ethyl selenoxide*

$\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}SeO$, a basic compound, forming crystallized salts. On adding hydrochloric acid to its solution *ethyl-selenium chloride* $(C_2H_5)_2SeCl_2$ separates as a heavy oil.

Ethyl Telluride $\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}Te$ is a reddish yellow liquid, possessing an intolerably nasty smell. It is soluble in nitric acid; on the addition of hydrochloric acid to this solution, *ethyl-tellurium chloride* $(C_2H_5)_2TeCl_2$ separates out, a colourless oil, which by treatment with silver oxide yields *ethyl-tellurium oxide* $(C_2H_5)_2TeO$, a crystalline solid, soluble in water, and possessing a faint alkaline reaction.

COMPOUNDS OF ETHYL WITH THE METALS.

ETHYL COMPOUNDS OF ZINC.

Zinc-ethyl or Zinc Ethide $\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}Zn$.—This important compound is most conveniently prepared by heating ethyl iodide with an excess of coarse zinc filings in a flask connected with a reversed condenser. The upper end of the condenser is provided with a long descending tube dipping under mercury; thus the entrance of air in the apparatus is prevented, and the reaction proceeds quicker under the increased pressure. The end of the reaction is recognized by iodide of ethyl ceasing to flow back from the condenser. The flask is now connected with the upper end of a condenser, and heated in an oil-bath as long as zinc-ethyl distils over, which must be collected in a receiver filled with dry carbon dioxide. It is absolutely necessary that the materials used, and all parts of the apparatus, be perfectly dry.

When zinc acts upon ethyl iodide the solid compound $\left.\begin{matrix}C_2H_5\\I\end{matrix}\right\}Zn$ is first formed, which at a higher temperature is decomposed with the formation of zinc-ethyl and zinc iodide, thus:—

$$\left.\begin{matrix}C_2H_5\\I\end{matrix}\right\}Zn + \left.\begin{matrix}I\\C_2H_5\end{matrix}\right\}Zn = \left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}Zn + \left.\begin{matrix}I\\I\end{matrix}\right\}Zn$$

It is necessary to employ the zinc in excess, because if an excess of ethyl iodide be present, the latter acts on the zinc ethyl and *butane* is formed:—

$$2\left.\begin{matrix}C_2H_5\\I\end{matrix}\right\} + \left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}Zn = 2C_4H_{10} + ZnI_2$$

Zinc-ethyl is a colourless mobile liquid, heavier than water, and possessing a peculiar disagreeable odour. It boils at 118°, and takes fire in the air, burning with a bright greenish flame, giving off thick clouds of zinc oxide. When air is slowly admitted *zinc ethylate* $(C_2H_5O)_2Zn$ is formed, a white solid, which is acted upon by water with the formation of ethyl alcohol and zinc hydroxide. Water decomposes zinc-ethyl violently, ethane being given off:—

$$\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}Zn + 2\left.\begin{matrix}H\\H\end{matrix}\right\}O = 2C_2H_6 + Zn(OH_2)$$

On passing dry ammonia into zinc-ethyl, zincamide, a white solid, and ethane are formed:—

$$\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}Zn + 2NH_3 = Zn(NH_2)_2 + 2C_2H_6$$

The property of zinc-ethyl to undergo readily double decompositions with a great number of other bodies, is frequently made use of in the preparation of ethyl compounds. Several examples have already been given, and others will be mentioned hereafter.

Sodium and potassium dissolve in zinc-ethyl, a crystalline double compound, as $C_2H_5Na + (C_2H_5)_2Zn$, being formed, from which the sodium (or potassium) ethide has not yet been isolated. On passing dry carbon dioxide over it, sodium propionate is formed:—

$$C_2H_5Na + CO_2 = C_2H_5.CO_2Na$$

ETHYL COMPOUNDS OF MERCURY.

Mercury-diethyl or Mercuric Ethide $\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}Hg$ is obtained from sodium amalgam, ethyl iodide, and acetic ether in the same way as zinc methyl from methyl iodide. It is a very heavy, colourless liquid, boiling at 159°, and possessing a disagreeable smell. When it is exposed to the air it is not altered, and on heating it with zinc, zinc-ethyl is formed, whilst with aluminium it gives *aluminium-ethyl* $Al(C_2H_5)_3$, a colourless liquid, fuming in the air, and taking fire when exposed in a thin layer. On adding mercury-ethyl to a solution of iodine in alcohol, *mercuric iodethide* C_2H_5HgI is formed, which crystallizes in silvery scales:—

$$\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}Hg + I_2 = C_2H_5I + \left.\begin{matrix}C_2H_5\\I\end{matrix}\right\}Hg$$

Mercuric Chlorethide C_2H_5HgCl is obtained by mixing mercury-ethyl with an alcoholic solution of mercuric chloride. It crystallizes in shining scales, and yields, by acting on it with freshly precipitated moist silver oxide, the hydroxide $\left.\begin{matrix}C_2H_5\\HO\end{matrix}\right\}Hg$, a colourless and strongly alkaline liquid, which forms salts with acids. By the action of concentrated sulphuric acid on mercury-ethyl ethane is formed, and *mercuric sulphatethide* $(C_2H_5Hg)_2SO_4$, crystallizing from alcohol in large colourless plates.

ETHYL COMPOUNDS OF TIN.

Tin-diethyl or Stannous Ethide $\left.\begin{matrix}(C_2H_5)_2Sn\\(C_2H_5)_2Sn\end{matrix}\right\}$ is obtained, together with tin-triethyl, when an alloy of tin and sodium is heated with ethyl iodide. It is a colourless, oily liquid, which on heating is decomposed into metallic tin and stannic ethide. Stannous ethide is a dyad radical. When exposed to the air it combines with oxygen, forming *stannic oxethide* $(C_2H_5)_2SnO$, an amorphous white powder, forming salts with acids. Stannous ethide also readily combines with the elements of the chlorine group. The compounds thus obtained crystallize well, and are soluble in water and alcohol; on adding a caustic alkali to the solution, stannic oxethide is precipitated.

Tin-triethyl or Stannoso-stannic Ethide $\left.\begin{matrix}(C_2H_5)_3Sn\\(C_2H_5)_3Sn\end{matrix}\right\}$ is a thin liquid which is easily separated from stannous ethide; the latter being readily soluble in alcohol, whilst tin-triethyl is insoluble; it is decomposed on heating. With oxygen it forms the compound $\left.\begin{matrix}(C_2H_5)_3Sn\\(C_2H_5)_3Sn\end{matrix}\right\}O$, a white solid possessing a strong, penetrating smell, and forming salts: thus, on adding hydrochloric acid the chloride $(C_2H_5)_3SnCl$ is obtained, a liquid boiling at 210°, and possessing a very pungent smell.

Tin-tetrethyl or Stannic Ethide $\left.\begin{matrix}C_2H_5\\C_2H_5\\C_2H_5\\C_2H_5\end{matrix}\right\}Sn$ is formed by the action of zinc-ethyl upon anhydrous stannic chloride or the chlorides $(C_2H_5)_2SnCl_2$ and $(C_2H_5)_3SnCl$, as well as by heating stannous ethide. It is a colourless liquid with a faint ethereal smell, boiling at 181°. It does not absorb oxygen, but is readily inflammable, and burns with a bright luminous flame. By the action of iodine it yields ethyl iodide and stannic iodo-triethide $(C_2H_5)_3SnI$, and when it is heated with fuming hydrochloric acid ethane escapes, and stannic chloro-triethide is left behind.

ETHYL COMPOUNDS OF LEAD.

Lead-tetrethyl or Plumbic Ethide $\left.\begin{matrix}C_2H_5\\C_2H_5\\C_2H_5\\C_2H_5\end{matrix}\right\}Pb$ is formed, together with lead-triethyl, by acting on lead chloride with zinc-ethyl:—

$$Pb_2Cl_4 + 2Zn(C_2H_5)_2 = 2ZnCl_2 + Pb + Pb(C_2H_5)_4$$

It is a colourless heavy liquid, boiling at 200°. It does not fume in the air, but is easily inflammable, burning with a yellow, green-bordered flame. By fuming hydrochloric acid it is decomposed into ethane and *plumbic chloro-triethide* $(C_2H_5)_3PbCl$, crystallizing in long needles, and possessing a pungent smell like mustard.

Lead-triethyl $\left.\begin{matrix}(C_2H_5)_3Pb\\(C_2H_5)_3Pb\end{matrix}\right\}$ is a thin liquid which is decomposed on heating. To prepare it, an alloy of lead and sodium, $PbNa_3$, is heated with ethyl iodide, and, after cooling, the product exhausted with ether. It absorbs oxygen from the air, forming a solid oxide having basic properties and yielding crystallized salts.

COMPOUNDS OF ETHYL AND SILICON.

Silicon Ethide $\left.\begin{matrix}C_2H_5\\C_2H_5\\C_2H_5\\C_2H_5\end{matrix}\right\}Si$ is obtained by the action of zinc-ethyl upon silicon tetrachloride. It is a colourless liquid, boiling at 150°, and a very stable compound, not being oxidized even by nitric acid. With chlorine it yields substitution-products; the first product being *monochlorosilicon-ethyl* $SiC_8H_{19}Cl$, a colourless liquid boiling at 150°. This compound shows in all its reactions great resemblance to the chlorides of the alcohol radicals. Thus, on heating it with potassium acetate an acetic ether is formed, which on treatment with caustic potash yields an alcohol, a liquid smelling like camphor. Silicon ethide may therefore be considered as nonane or nonyl hydride, in which one atom of carbon is replaced by one of silicon; by substituting one atom of hydrogen by other radicals, compounds of the monad radical *siliconoyl* SiC_8H_{19} are formed :—

		Boiling-point.
Siliconethyl or Siliconane	SiC_8H_{20}	150°
Silicononyl Chloride	$SiC_8H_{19}Cl$	187
Silicononyl Acetate	$\left.\begin{matrix}SiC_8H_{19}\\C_2H_3O\end{matrix}\right\}O$	211
Silicononyl Alcohol	$\left.\begin{matrix}SiC_8H_{19}\\H\end{matrix}\right\}O$	190

Silicopropionic Acid $C_2H_5.SiO.OH$.—By acting with zinc-ethyl and sodium upon $SiCl(OC_2H_5)_3$ (a compound described under Ethyl Silicate), the body $SiC_2H_5(OC_2H_5)_3$ is formed, which has been called *ethyl orthosilicopropionate.* It is a colourless liquid, boiling at 158°·5. When it is heated with acetyl chloride to 180° ethyl acetate is formed, and *siliconmonethyl trichloride* $SiC_2H_5Cl_3$, a liquid fuming in the air, and which is easily decomposed by water with the formation of silicopropionic acid, a white light amorphous powder, which has the greatest resemblance to finely divided silica. It dissolves in concentrated potash solution, and is not precipitated by hydrochloric acid; but on boiling the alkaline solution down with sal ammoniac, silicopropionic acid is left behind in the insoluble state. It differs from silica, however, by not being soluble in caustic soda; and moreover on heating it, it begins to glow, an inflammable gas being evolved. Silicopropionic acid is the first example of a new class of acids containing SiO.OH in the place of carboxyl CO.OH.

Silicoheptyl Compounds.—By the further action of zinc-ethyl and sodium upon silicopropionic ether, first *silicondiethyl ether* $Si(C_2H_5)_2(OC_2H_5)_2$ is formed, a liquid boiling at 155·8°, which in appearance and smell is very similar to silicic ether. On very prolonged treatment with sodium and zinc-ethyl, *silicoheptyl ether* $Si(C_2H_5)_3OC_2H_5$, a liquid boiling at 153°, is produced. On heating with acetyl chloride to 180° it yields ethyl acetate and *silicontriethyl chloride*, or *silicoheptyl chloride* $Si(C_2H_5)_3Cl$, a liquid having a pungent and camphor-like smell, and boiling at 143·5°. It is readily decomposed by aqueous ammonia, with the formation of *silicon triethylhydroxide* or *tertiary silicoheptyl alcohol* $Si(C_2H_5)_3OH$. This body may be regarded as triethyl carbinol, in which one atom of carbon is replaced by silicon, and may therefore be called *triethyl silicol*, It is a colourless liquid, smelling like camphor, and boiling at 154°.

By the action of fuming sulphuric acid on triethyl silicol it is oxidized with the formation of silicopropionic acid and ethene:—

$$Si(C_2H_5)_3OH + 2SO_3 = Si(C_2H_5)O.OH + 2C_2H_4 + 2SO_2 + H_2O$$

When silicoheptyl ether is heated with hydriodic acid it yields ethyl iodide and *silicoheptyl oxide* $\left.\begin{matrix}Si(C_2H_5)_3\\ Si(C_2H_5)_3\end{matrix}\right\}O$, a colourless liquid, boiling at 231°.

Sodium acts violently on a solution of triethyl silicol in pure ether, the compound $Si(C_2H_5)_3ONa$ being formed, which is a white powder. By passing dry carbon dioxide into its ethereal solution, a white precipitate is produced of *sodium silicoheptyl-carbonate* $Si(C_2H_5)_3O.CO.ONa$. It is very deliquescent, and is resolved by water into triethyl silicol and sodium carbonate. When heated to redness it is resolved into silicoheptyl oxide and sodium carbonate, being the first silicon-containing body that leaves carbonate instead of silicate when heated.

ETHANE AND ITS SUBSTITUTION-PRODUCTS.

Ethane C_2H_6 is a colourless gas, which, as we have just seen, may be obtained by different reactions. Pure ethane is formed by passing a galvanic current through a concentrated solution of potassium acetate; the gas must be washed with caustic potash and concentrated sulphuric acid, to free it from carbon dioxide and other admixtures. It is also formed by heating dry methyl iodide with zinc in closed tubes to 150°, or by decomposing zinc-ethyl with water, or mercuric ethide with sulphuric acid.

When a mixture of equal volumes of ethane and chlorine is exposed to the daylight, ethyl chloride and dichlorethane $C_2H_4Cl_2$ are formed. By the further action of chlorine the following products are formed:—

	Boiling-point.		Boiling-point.
C_2H_5Cl	12·5°	$C_2H_2Cl_4$	127°
$C_2H_4Cl_2$	59	C_2HCl_5	158
$C_2H_3Cl_3$	75	C_2Cl_6	180

Dichlorethane will be described further on.

Trichlorethane $C_2H_3Cl_3$ is acted upon by an alcoholic solution of caustic potash, the products being potassium chloride and potassium acetate:—

$$\begin{array}{l}CH_3\\ |\\ CCl_3\end{array} + 4KOH = \begin{array}{l}CH_3\\ |\\ CO.OK\end{array} + 3KCl + 2H_2O$$

Hexachlorethane C_2Cl_6, commonly called carbon sesquichloride, forms colourless crystals and smells like camphor.

ACETYL COMPOUNDS.

Acetaldehyde C_2H_4O, commonly called simply aldehyde (from alcohol dehydrogenatum), as it was the first known of this class of bodies, is obtained by oxidizing spirits of wine by means of manganese dioxide and sulphuric acid, chromic acid, or platinum black, in presence of air, or if alcohol or ether are burning without a sufficient supply of air. It is also formed by heating a mixture of acetate and formate of calcium:—

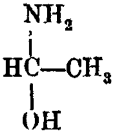
$$\left\{\begin{array}{l}H\\ CO\\ OH\end{array}\right. + \left\{\begin{array}{l}CH_3\\ CO\\ OH\end{array}\right. = \left\{\begin{array}{l}CH_3\\ CO\\ H\end{array}\right. + CO_2 + H_2O$$

It is contained in considerable quantity in the first runnings obtained in the manufacture of spirits of wine.

To prepare pure aldehyde, three parts of potassium dichromate in small pieces are placed in a flask, surrounded by a freezing mixture, and a well-cooled mixture of two parts of spirits of wine, four parts of sulphuric acid, and twelve parts of water added. After connecting the flask with a condenser, the freezing mixture is removed; a violent reaction very soon sets in, and the liquid begins to boil. The vapours have first to pass through an ascending tube surrounded by warm water at about 50°. Alcohol and different products are condensed and flow back, whilst the vapour of the aldehyde, after having passed through a descending condenser, is absorbed in anhydrous ether. On passing dry ammonia gas into the ethereal solution, a white crystalline solid, called *aldehyde-ammonia* $C_2H_4O.NH_3$ separates. On distilling this substance with dilute sulphuric acid, pure aldehyde is obtained, which may be dried over calcium chloride. Acetaldehyde is a colourless liquid, boiling at 21°, and having a very pungent and suffocating smell. It is readily soluble in water; caustic potash transforms it into a brown resinous mass. Like all aldehydes it is very easily oxidized, and acts therefore as a powerful reducing agent. Thus, on heating it with a little ammonia and nitrate of silver, metallic silver separates out, coating the sides of the vessel with a bright mirror :—

$$C_2H_4O + Ag_2O = C_2H_4O_2 + Ag_2$$

It combines with ammonia, and forms a crystalline compound, which has a peculiar smell of mice. The constitution of *aldehyde-ammonia* is the following :—



$$\begin{array}{c} NH_2 \\ | \\ HC—CH_3 \\ | \\ OH \end{array}$$

By dilute acids it is decomposed, aldehyde being liberated and an ammonium salt formed. When kept in the moist state it undergoes a slow decomposition, and is changed into a brown syrupy liquid, which contains a basic compound called *aldehydine* or *hydracetamide* $C_6H_{12}N_2$:—

$$3(C_2H_4O.NH_3) = C_6H_{12}N + NH_3 + 3H_2O$$

Aldehydine is an amorphous mass, soluble in water, and possessing an alkaline reaction. It combines with acids, forming amorphous salts. On boiling its aqueous solution ammonia escapes, and a new base, *oxytrialdine* $C_6H_{11}NO$, is obtained, which possesses properties very similar to those of aldehydine.

If aldehyde-ammonia is heated with alcohol, the bases *oxytetraldine* $C_8H_{13}NO$ and *oxypentaldine* $C_{10}H_{15}NO$ are obtained.

Aldehyde combines with the acid sulphites of the alkali-metals, and forms crystalline compounds, which are not very soluble in water; thus if aldehyde is shaken with a cold concentrated solution of acid sodium sulphite, the liquid is converted into a *magma* of crystals having the formula $CH_3.CH\left\{\begin{matrix}OH\\SO_3Na\end{matrix}\right.$. Dilute acids or alkalis again liberate aldehyde from these compounds.

With anhydrous prussic acid, aldehyde forms the compound

$C_2H_4O.CNH$, which boils at 180°, with partial decomposition. On adding concentrated hydrochloric acid to this body ammonium chloride and lactic acid are formed (compare lactic acid).

Phosphorus pentachloride acts violently upon aldehyde; the products of the reaction being phosphorus oxychloride and *dichlorethane* $C_2H_4Cl_2$.

A great number of substances, such as hydrochloric acid, sulphuric acid, carbonyl chloride, &c., even if present only in very minute quantities, cause the condensation of the aldehyde into *paraldehyde* $C_6H_{12}O_6$, a liquid boiling at 124°, and solidifying at a low temperature into crystals melting at + 10·5°. On distilling paraldehyde with the above substances, it again splits up into three molecules of acetaldehyde.

Another polymeride called *metaldehyde*, the molecular weight of which is not known, is produced when the above-mentioned substances are brought into contact with aldehyde at a temperature below 0°. It crystallizes in colourless needles or prisms, which when quickly heated sublime. When metaldehyde is heated in a closed vessel to 115°, it again changes after a few hours into common aldehyde.

On heating aldehyde with a solution of zinc chloride or some other salts, water is eliminated, and *croton aldehyde* C_4H_6O is formed, a compound which will be described hereafter.

ACETIC ACID $C_2H_4O_2$.

Dilute acetic acid, or vinegar, has been known from very early times. The different modes of the formation of this acid have already been fully described. On the large scale acetic acid is produced by the oxidation of alcohol, or by the destructive distillation of wood. Pure alcohol, even when very dilute, is not oxidized in contact with air, but in the presence of platinum black and air it is converted into aldehyde and acetic acid. The same change occurs when dilute alcohol contains certain nitrogenous organic bodies. For this reason wine, beer, &c., in which such bodies are contained, turn sour on exposure to the air.

In the manufacture of vinegar a mixture of wine, beer, or diluted spirits, with some vinegar and yeast, is kept in loosely covered vats, at a temperature of about 24°—27°, for about fourteen days, after which time the liquid is changed into vinegar. On increasing the surface of the liquid, the oxidation goes on much quicker. To effect this the liquid is made to run slowly over shavings of beechwood saturated with vinegar, contained in large vats, through which a current of air is made to pass.

Acetic acid is found in nature in the form of acetic ethers in several plants; it has also been found in small quantities in animal juices.

The so-called pyroligneous acid, obtained by the distillation of wood, is dilute acetic acid mixed with empyreumatic substances. It is used to prepare the common commercial acetic acid, by neutralizing it with lime, and evaporating the solution to dryness; the residue is gently roasted so as to destroy the foreign matters, and then distilled with hydrochloric acid.

. To obtain pure acetic acid, five parts of anhydrous fused sodium acetate are distilled with six parts of pure concentrated sulphuric acid. It is a colourless liquid, boiling at 118°, and solidifying on cooling into large transparent plates (*glacial acetic acid*) melting at + 17°. It possesses a pungent and sour smell, and is corrosive, destroying the skin. It mixes with water in all proportions, and is a solvent for essential oils, hydrocarbons, and many other bodies which are insoluble in water. At 15° it has the spec. grav. 1·0553. On mixing with water a contraction first takes place until 20—23 per cent. of water are present; this acid has the specific gravity 1·0748. On further addition of water the specific gravity diminishes again; acetic acid of 43 per cent. having the same specific gravity as the anhydrous acid.

Potassium Acetate $\left.\begin{matrix}C_2H_3O\\K\end{matrix}\right\}O$ is obtained by neutralizing dilute acetic acid with purified potassium carbonate. It is a very deliquescent salt, and difficult to crystallize. The dry salt fuses at 300°, and may be heated even stronger without undergoing decomposition. On cooling it solidifies to a radiated crystalline mass. If it is dissolved in common strong acetic acid, and the solution heated, water is given off, and a compound $\left.\begin{matrix}C_2H_3O\\K\end{matrix}\right\}O + \left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O$ (so called biacetate of potash) formed, which on heating to 200° splits up into anhydrous acetic acid and potassium acetate. This reaction may be used for preparing pure acetic acid.

Sodium Acetate is obtained on the large scale by dissolving the roasted crude calcium acetate in water, and decomposing it by sodium sulphate. The filtrate yields on evaporation sodium acetate, which if strongly heated may be freed from all traces of empyreumatic substances still adhering to it. Sodium acetate crystallizes in long monoclinic prisms $\left.\begin{matrix}C_2H_3O\\Na\end{matrix}\right\}O + 3H_2O$, which melt on heating, and give off water. The anhydrous salt fuses above 300° to a colourless clear liquid.

Ammonium Acetate $\left.\begin{matrix}C_2H_3O\\NH_4\end{matrix}\right\}O$.—The anhydrous salt is formed by passing dry ammonia into pure acetic acid. It is very soluble in water. On heating it decomposes into water and acetamide $C_2H_3O.NH_2$.

Aluminium Acetate is prepared by adding a solution of lead acetate to a solution of aluminium sulphate; it is used under the name of "red liquor," as a mordant in calico-printing.

By dissolving iron turnings in pyroligneous acid a solution of ferrous acetate is obtained called "iron liquor" which is also employed as a mordant.

Lead Acetate, commonly called *sugar of lead*, $Pb(C_2H_3O_2)_2 + 3H_2O$, is manufactured by dissolving litharge in dilute acetic acid; it crystallizes in monoclinic prisms, and is readily soluble in water. Its solution has the power of dissolving large quantities of litharge, basic salts such as $\left.\begin{matrix}C_2H_3O_2\\HO\end{matrix}\right\}Pb$ being formed, the solutions of which have a strong alkaline reaction, and are used for surgical purposes.

Cupric Acetate.—The so-called "verdigris," which is prepared on the large scale by bringing the marc of grapes in contact with copper-sheeting, is a mixture of basic salts, and consists chiefly of $\left.\begin{matrix}C_2H_3O_2\\HO\end{matrix}\right\}Cu$. By dissolving it in acetic acid, the normal acetate $Cu(C_2H_3O_2)_2 + H_2O$, crystallizing in rhombic prisms, is obtained.

The beautiful green pigment called "emerald green" is a double salt of copper acetate and arsenite $\left.\begin{matrix}2AsO_3\\C_2H_3O_2\end{matrix}\right\}Cu_2$, and is prepared by adding acetic acid to copper arsenite.

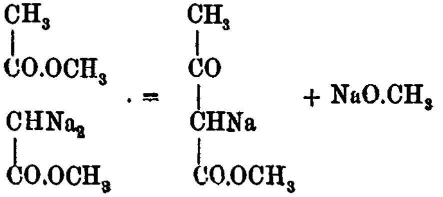
Silver Acetate $\left.\begin{matrix}C_2H_3O\\Ag\end{matrix}\right\}O$.—Silver nitrate precipitates from a solution of an acetate this salt as a white crystalline powder, which crystallizes from boiling water in flat, flexible, white, shining needles.

Methyl Acetate $\left.\begin{matrix}C_2H_3O\\CH_3\end{matrix}\right\}O$ is a mobile liquid having a refreshing smell, boiling at 55°. It is contained in crude wood spirits. To prepare it a mixture of methyl alcohol and sulphuric acid is distilled with dry sodium acetate. This ether has the same boiling-point as its metameride ethyl formate. Both can, however, be easily distinguished from each other; by treatment with alkalis, methyl acetate yields methyl alcohol and an alkaline acetate, whilst ethyl formate gives ethyl alcohol and an alkaline formate.

Ethyl Acetate $\left.\begin{matrix}C_2H_3O\\C_2H_5\end{matrix}\right\}O$, a liquid known by the name of "acetic ether," is best prepared in the following manner. To 9 parts of concentrated sulphuric acid 3·6 parts of commercial absolute alcohol are added by means of a funnel tube which reaches the bottom of the vessel, at the same time keeping the liquid well stirred. After standing for twenty-four hours this mixture is added to 6 parts of sodium acetate, which has previously been fused and broken into small fragments, and after twelve hours the mixture is distilled. Thus 6 parts of pure acetic ether are obtained, from which, by rectifying over calcium chloride, traces of water are removed. Ethyl acetate boils at 74°, and possesses a very pleasant and refreshing smell. It dissolves in about 11 parts of water; the solution soon assumes an acid reaction, the ether being decomposed into alcohol and acetic acid. Acetic ether is also slowly formed by allowing a mixture of acetic acid and alcohol to stand for some time, the refreshing smell of hock-vinegar being due to an admixture of this ether.

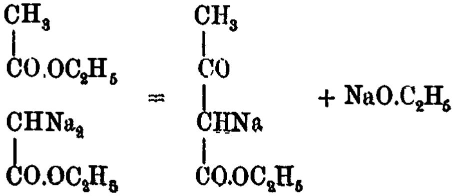
Sodium has a very peculiar action upon the acetates of methyl and ethyl. As far as this very complicated reaction has been studied, the first stage is that in the methyl group of acetyl one atom of hydrogen after the other is substituted by sodium; but little or no hydrogen is set free, probably because it acts in the nascent state upon some of the acetyl. The sodium compounds thus formed are again acted upon by the excess of the acetic ethers, the product of the reaction consisting of a white solid, from which two crystallinic compounds have been isolated, which have been formed according to the following equations:—

(1)



$$\begin{array}{l} CH_3 \\ | \\ CO.OCH_3 \\ \\ CHNa_2 \\ | \\ CO.OCH_3 \end{array} = \begin{array}{l} CH_3 \\ | \\ CO \\ | \\ CHNa \\ | \\ CO.OCH_3 \end{array} + NaO.CH_3$$

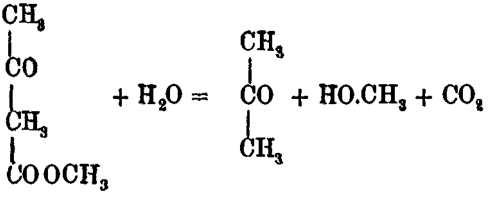
(2)



$$\begin{array}{l} CH_3 \\ | \\ CO.OC_2H_5 \\ \\ CHNa_2 \\ | \\ CO.OC_2H_5 \end{array} = \begin{array}{l} CH_3 \\ | \\ CO \\ | \\ CHNa \\ | \\ CO.OC_2H_5 \end{array} + NaO.C_2H_5$$

On adding a dilute acid to the first of these bodies, sodium is replaced by hydrogen, and a liquid boiling at 170° is obtained, which has been called *methyl-diacetic acid*, although the body is not an acid, but the methyl ether of an acid which is not known in the free state and which has been called *acetone-carbonic acid*.

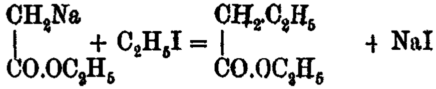
This ether, as well as the sodium compound, yield, when heated with water, carbon dioxide, methyl alcohol, and acetone (dimethyl-ketone):—



$$\begin{array}{l} CH_3 \\ | \\ CO \\ | \\ CH_2 \\ | \\ CO\,OCH_3 \end{array} + H_2O = \begin{array}{l} CH_3 \\ | \\ CO \\ | \\ CH_3 \end{array} + HO.CH_3 + CO_2$$

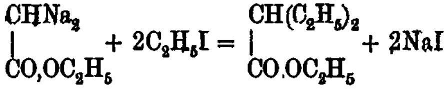
The compound obtained from ethyl acetate yields under the same circumstances *ethylacetone-carbonate* (ethyl-diacetic acid), which boils at 187°, and with water yields ethyl alcohol, acetone, and carbon dioxide.

If the solid product obtained by the action of sodium upon acetic ether is acted upon by ethyl iodide, different compounds are formed, which can be separated by fractional distillation; amongst them there are ethers of the fatty acids, such as *ethyl-acetic acid* or *butyric acid*, *which is* produced by the substitution of ethyl for one atom of hydrogen in the methyl group of acetic acid, the radical methyl being thus changed into propyl :—



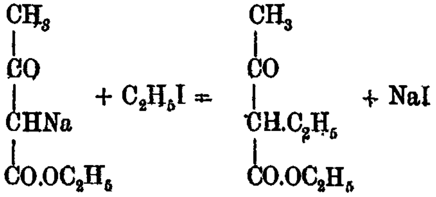
$$\begin{array}{l}CH_2Na\\ |\\ CO.OC_2H_5\end{array} + C_2H_5I = \begin{array}{l}CH_2.C_2H_5\\ |\\ CO.OC_2H_5\end{array} + NaI$$

In a similar way *diethyl-acetic acid*, an isomeride of caproic acid, is obtained:—



$$\begin{array}{l}CHNa_2\\ |\\ CO,OC_2H_5\end{array} + 2C_2H_5I = \begin{array}{l}CH(C_2H_5)_2\\ |\\ CO.OC_2H_5\end{array} + 2NaI$$

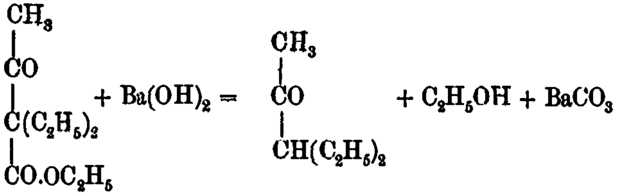
Another class of compounds are formed by the action of ethyl iodide upon the sodacetone-carbonic ethers :—



$$\begin{array}{l}CH_3\\ |\\ CO\\ |\\ CHNa\\ |\\ CO.OC_2H_5\end{array} + C_2H_5I = \begin{array}{l}CH_3\\ |\\ CO\\ |\\ CH.C_2H_5\\ |\\ CO.OC_2H_5\end{array} + NaI$$

The *ethyl ethacetone-carbonate* thus formed is readily decomposed by baryta-water, the products being alcohol, barium, carbonate, and methyl-propyl ketone $CO\left\{\begin{matrix}CH_3\\ C_3H_7\end{matrix}\right.$.

By a similar reaction *disodacetone-carbonic ether* yields *ethyl diethacetone-carbonate*, which is attacked by baryta-water in a similar way as the preceding compound.—



$$\begin{array}{l}CH_3\\ |\\ CO\\ |\\ C(C_2H_5)_2\\ |\\ CO.OC_2H_5\end{array} + Ba(OH)_2 = \begin{array}{l}CH_3\\ |\\ CO\\ |\\ CH(C_2H_5)_2\end{array} + C_2H_5OH + BaCO_3$$

Acetyl Chloride C_2H_3OCl.—The best method to prepare this compound is to mix gradually acetic acid and phosphorus trichloride, and to distil the mixture from a water-bath :—

$$3\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O + PCl_3 = 3C_2H_3.OCl + PO_3H_3$$

It is a colourless liquid, boiling at 55°, and possessing a very pungent smell; it fumes in the air, and is heavier than water, by which it is rapidly decomposed into acetic acid and hydrochloric acid.

Acetyl Bromide C_2H_3OBr, obtained by the action of phosphorus tribromide upon acetic acid, has similar properties; it boils at 81°.

If sodium amalgam is brought into contact with a mixture of acetyl chloride and acetic acid, the nascent hydrogen converts the chloride first into aldehyde, which combines with hydrogen to form alcohol; the latter is again acted upon by acetyl chloride, the products of the reaction thus being sodium chloride, sodium acetate, acetic ether, and water.

On heating acetyl chloride with silver cyanide, *acetyl cyanide* $CH_3.CO.CN$ is obtained, a liquid boiling at 91°, and which by water is decomposed into acetic acid and hydrocyanic acid.

Acetyl Oxide or Acetic Anhydride $\left.\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\right\}O$ is formed by the action of acetyl chloride upon any anhydrous acetate. To prepare it, phosphorus oxychloride is added drop by drop to an excess of fused sodium acetate; a violent reaction ensues, by which sufficient heat is evolved to volatilize the anhydride, which is formed by the two successive reactions :—

$$(1)\quad POCl_3 + 3\left.\begin{matrix}C_2H_3O\\Na\end{matrix}\right\}O = 3\left.\begin{matrix}C_2H_3O\\Cl\end{matrix}\right\} + PO_4Na_3$$

$$(2)\quad \left.\begin{matrix}C_2H_3O\\Cl\end{matrix}\right\} + \left.\begin{matrix}C_2H_3O\\Na\end{matrix}\right\}O = \left.\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\right\}O + NaCl$$

It is a colourless liquid, boiling at 138°, and possessing a pungent smell. It is heavier than water, by which it is decomposed—slowly in the cold, more quickly on heating—into two molecules of acetic acid :—

$$\left.\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\right\}O + \left.\begin{matrix}H\\H\end{matrix}\right\}O = \left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O + \left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O$$

Acetic anhydride combines with potassium acetate, forming a crystalline compound $C_4H_6O_3 + 2C_2H_3O_2K$. By the action of hydrochloric acid it yields acetic acid and acetyl chloride :—

$$\left.\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\right\}O + \left.\begin{matrix}H\\Cl\end{matrix}\right\} = \left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O + \left.\begin{matrix}C_2H_3O\\Cl\end{matrix}\right\}$$

By treating it with iodine and phosphorus *acetyl, iodide* C_2H_3OI is obtained, a liquid having a brown colour, and boiling at 108°. By water it is decomposed into acetic acid and hydriodic acid.

If silicon tetrachloride is digested with a mixture of acetic acid and acetic anhydride, *acetyl silicon oxide* or *silico-acetic anhydride* $Si(C_2H_3O_2)_4$ is formed:—

$$4\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O + SiCl_4 = (C_2H_3O_2)_4Si + 4HCl$$

It forms beautifully white crystals, which if thrown into water decompose with a hissing noise, acetic acid and silicic acid being formed.

If acetic anhydride is heated with ethyl silicate a reaction sets in by which ethyl acetate and *triethyl-acetyl silicate* are formed:—

$$Si(OC_2H_5)_4 + \left.\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\right\}O = Si\left\{\begin{matrix}OC_2H_5\\OC_2H_5\\OC_2H_5\\OC_2H_3O\end{matrix}\right. + \left.\begin{matrix}C_2H_3O\\C_2H_5\end{matrix}\right\}O$$

Ethyl-acetyl silicate is a liquid, which has a faint smell of acetic acid, and boils at about 190°.

Acetyl Peroxide $\left.\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\right\}O_2$.—To obtain this compound, pure barium peroxide is added to a solution of acetic anhydride in ether; the liquid is separated from the barium acetate by filtration, and evaporated at a low temperature. The peroxide is left behind as a thick liquid, which on heating explodes with great violence. It has a burning taste, and is as powerful an oxidizing agent as hydrogen peroxide; it decolorizes indigo solution, sets iodine free from potassium iodide, and converts potassium ferrocyanide into ferricyanide. This substance is formed according to the equation:—

$$2\left.\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\right\}O + BaO_2 = \left.\begin{matrix}C_2H_3O_2\\C_2H_3O_2\end{matrix}\right\}Ba + \left.\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\right\}O_2$$

Thiacetic Acid $\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}S$ is obtained by distilling acetic acid with phosphorus pentasulphide:—

$$5\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O + P_2S_5 = 5\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}S + P_2O_5$$

Freshly prepared it is a colourless liquid, but after some time it becomes yellow; it boils at 93°, and smells like hydrogen sulphide and acetic acid. It is soluble in water, and forms crystalline salts, the most characteristic of which is *lead thiacetate*, which crystallizes from water in white needles which cannot be kept, as they soon decompose, leaving lead sulphide behind.

When phosphorus pentasulphide acts upon acetic anhydride, *acetyl sulphide* or *thiacetic anhydride* $\left.\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\right\}S$ is formed, a colourless liquid boiling at 121°, which with water yields acetic acid and thiacetic acid:—

$$\left.\begin{array}{l}C_2H_3O\\C_2H_3O\end{array}\right\}S+\left.\begin{array}{l}H\\H\end{array}\right\}O=\left.\begin{array}{r}C_2H_3O\\H\end{array}\right\}S+\left.\begin{array}{r}C_2H_3O\\H\end{array}\right\}O$$

Acetamide $\left.\begin{array}{c}C_2H_3O\\H\\H\end{array}\right\}N$ is slowly formed when acetic ether is acted upon by ammonia in the cold, quickly if they are heated together in sealed tubes to 120°. It forms white crystals, melting at 78°, boiling at 222°, and smelling like mice. It combines with acids, but its salts are not very stable; the nitrate $N(C_2H_3O)H_3.NO_3$ is obtained in form of crystalline plates by evaporating a solution of acetamide in nitric acid. Freshly precipitated silver oxide dissolves in a hot aqueous solution of acetamide, and on cooling colourless crystals of *silver acetamide* $\left.\begin{array}{c}C_2H_3O\\H\\Ag\end{array}\right\}N$ separate. Mercuric oxide forms a similar compound, *mercury acetamide* $\left.\begin{array}{c}(C_2H_3O)_2\\H_2\\Hg\end{array}\right\}N$.

When dry hydrochloric acid gas is passed over fused acetamide, *diacetamide* $\left.\begin{array}{c}C_2H_3O\\C_2H_3O\\H\end{array}\right\}N$ distils, and the residue consists of ammonium chloride and *acetdiamine hydrochloride* $C_2H_6N_2ClH$, a salt crystallizing in colourless needles. The free base itself has not been isolated; by adding an alkali to one of its salts, acetdiamine takes up water, and is resolved into ammonia and acetic acid.

The reactions by which this compound is formed are expressed by the following equations:—

$$(1)\quad 2\left.\begin{array}{c}C_2H_3O\\H\\H\end{array}\right\}N+HCl=NH_4Cl+\left.\begin{array}{r}C_2H_3O\\C_2H_3O\\H\end{array}\right\}N$$

$$(2)\quad \begin{array}{l}CH_3\\|\\CO.NH_2\end{array}+\begin{array}{l}CH_3\\|\\CO.NH_2\end{array}=\begin{array}{l}CH_3\\|\\CO.OH\end{array}+\begin{array}{l}CH_3\\|\\C(NH)NH_2\end{array}$$

If acetic ether is acted upon by ethylamine instead of ammonia, *ethyl-acetamide* $\left.\begin{array}{c}C_2H_3O\\C_2H_5\\H\end{array}\right\}N$ is obtained, a thick liquid boiling at 200°.

By acting upon acetamide or ammonium acetate with phosphorus pentoxide, water and *acetonitrile* (methyl cyanide) are formed:—

$$\begin{array}{l}CH_3\\|\\CO.NH_2\end{array}=\begin{array}{l}CH_3\\|\\CN\end{array}+H_2O$$

In a similar manner it is acted upon by phosphorus pentasulphide:—

$$5\left.\begin{matrix}CH_2.CO\\H_2\end{matrix}\right\}N + P_2S_5 = 5CH_3.CN + 5H_2S + P_2O_5$$

Diacetamide $\left.\begin{matrix}C_2H_3O\\C_2H_3O\\H\end{matrix}\right\}N$.—Besides the reaction mentioned above this compound is also formed by heating acetonitrile with acetic acid:—

$$NC.CH_3 + O\left\{\begin{matrix}CO.CH_3\\H\end{matrix}\right. = N\left\{\begin{matrix}CO.CH_3\\CO.CH_3\\H\end{matrix}\right.$$

It forms small white needles, melting at 74°; its aqueous solution has an acid reaction.

Triacetamide $\left.\begin{matrix}C_2H_3O\\C_2H_3O\\C_2H_3O\end{matrix}\right\}N$.—This compound is formed, but slowly, on heating acetonitrile with acetic anhydride to 200°:—

$$NC.CH_3 + O\left\{\begin{matrix}CO.CH_3\\CO.CH_3\end{matrix}\right. = N\left\{\begin{matrix}CO.CH_3\\CO.CH_3\\CO.CH_3\end{matrix}\right.$$

It has great resemblance with diacetamide, forming white crystals melting at 78°, and dissolving in water to a neutral liquid.

SUBSTITUTION-PRODUCTS OF ACETIC ACID.

Monochloracetic Acid $\left.\begin{matrix}CH_2Cl.CO\\H\end{matrix}\right\}O$.—This acid is best prepared by passing chlorine into boiling acetic acid in the presence of iodine. It is also formed by acting with chlorine upon acetic anhydride at 100°:—

$$\left.\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\right\}O + Cl_2 = \left.\begin{matrix}C_2H_2ClO\\H\end{matrix}\right\}O + \left.\begin{matrix}C_2H_3O\\Cl\end{matrix}\right\}$$

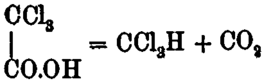
Monochloracetic acid crystallizes in rhombic prisms, melting at 62° and boiling at 185°; its vapour has a suffocating smell, attacking the eyes. It has a sharp, sour taste, and is very caustic, destroying the skin, and is therefore used for removing corns and warts. It is very readily soluble and deliquescent in moist air. The metallic chloracetates crystallize well; on boiling their aqueous solution they are resolved into a metallic chloride and *glycollic* or *oxy-acetic* acid

$\left.\begin{matrix}CH_2(OH)CO\\ H\end{matrix}\right\}O$. Nascent hydrogen easily reduces monochloracetic acid to acetic acid, and phosphorus trichloride converts it into *monochloracetyl chloride* $\left.\begin{matrix}CH_2Cl.CO\\ Cl\end{matrix}\right\}$, a compound which is also formed by the action of chlorine upon acetyl chloride. It is a colourless liquid, possessing a pungent and suffocating smell, and boiling at 105°. Water decomposes it into chloracetic acid and hydrochloric acid. With ethyl alcohol it yields *ethyl monochloracetate* $\left.\begin{matrix}CH_2Cl.CO\\ C_2H_5\end{matrix}\right\}O$, a liquid boiling at 143°·5, and possessing a pleasant smell. It is also formed by passing hydrochloric acid gas into an alcoholic solution of monochloracetic acid. By acting on this ether with ammonia, *monochloracetamide* $\left.\begin{matrix}CH_2Cl.CO\\ H_2\end{matrix}\right\}N$ is formed, which is soluble in water and crystallizes in shining scales.

Dichloracetic Acid $\left.\begin{matrix}CHCl_2.CO\\ H\end{matrix}\right\}O$ is obtained by the further action of chlorine on monochloracetic acid; it forms colourless crystals, and boils at 195°. *Potassium dichloracetate* $\left.\begin{matrix}CHCl_2.CO\\ K\end{matrix}\right\}O$ crystallizes from alcohol in large silky plates.

Trichloracetic Acid $\left.\begin{matrix}CCl_3.CO\\ H\end{matrix}\right\}O$.—This acid can be obtained in different ways. It is formed when an excess of chlorine acts on acetic acid in the sunlight, but the most convenient method to obtain it in large quantities is to oxidize chloral hydrate (see below) with fuming nitric acid. It is also produced by heating perchlorethyl oxide, which at 300° is resolved into *hexachlorethane* C_2Cl_6 and *triacetyl chloride* $\left.\begin{matrix}CCl_3.CO\\ Cl\end{matrix}\right\}$. The latter, in contact with water, yields hydrochloric acid and trichloracetic acid.

Trichloracetic acid crystallizes in colourless rhombohedrons and boils at 195°; it is very caustic, producing blisters on the skin, and it is very readily soluble in water. The trichloracetates are well defined salts; *lead trichloracetate* $Pb(C_2Cl_3O_2)_2+H_2O$ is readily soluble in water and forms large rhombic prisms; *copper trichloracetate* $Cu(C_2Cl_3O_2)_2 + 6H_2O$ can be easily obtained in large crystals resembling copper sulphate. On distilling the ammonium salt with phosphorus pentoxide, *trichloracetonitrile* C_2Cl_3N is formed, a colourless liquid boiling at 81°, which, by means of caustic potash, can be reconverted into trichloracetic acid. On heating this acid with alkalis it splits up into chloroform and carbon dioxide:—



$$\begin{matrix}CCl_3\\ |\\ CO.OH\end{matrix} = CCl_3H + CO_2$$

Chloral or Trichloracetaldehyde C_2Cl_3OH is obtained by passing dry chlorine into absolute alcohol as long as any action takes place. The final product, however, is not chloral, but a solid compound of chloral and alcohol called *chloral alcoholate*, which is decomposed by concentrated sulphuric acid into alcohol and chloral:—

$$CCl_3.CH\left\{\begin{matrix}OH\\OC_2H_5\end{matrix}\right. = CCl_3.COH + C_2H_5.OH$$

The reaction by which chloral alcoholate is produced is rather complicated. First aldehyde is formed, which combines with some of the alcohol, forming *acetal* $CH_3.CH(OC_2H_5)_2$, a compound which will be described under ethidene compounds. By the action of chlorine on acetal, it is next converted into *trichloracetal*, which by the hydrochloric acid produced is resolved into chloral alcoholate and ethyl chloride:—

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

Chloral is also formed by the action of chlorine upon aldehyde; it is a colourless liquid, possessing a peculiar irritating smell, and boiling at 99°. Like common aldehyde, it reduces silver from an ammoniacal solution of the nitrate, and forms crystalline compounds with ammonia and the acid sulphites of the alkali-metals. Hydrogen in the nascent state converts it into aldehyde, and oxidizing agents transform it into trichloracetic acid. It combines with water, with the evolution of heat, forming *chloral hydrate* $CCl_3.CH(OH)_2$, white transparent monoclinic crystals boiling at 120°; concentrated sulphuric acid again resolves this body into water and chloral. Chloral also combines with alcohols, with acetamide and other amides, and with urea. By the action of aqueous alkalis it splits up into chloroform and formic acid:—

$$CCl_3.COH + KOH = CCl_3H + COH.OK$$

Chloral undergoes polymerization on standing for some time, *metachloral* being formed, a white porcelain-like mass; this change takes place much quicker in presence of a little sulphuric acid. On heating metachloral to 180° it is again transformed into chloral.

Chloral hydrate is used as a very valuable medicine; it acts as a sedative and antispasmodic, producing anæsthesia and a quiet sleep. By adding a little water to a mixture of chloral hydrate and potassium cyanide, and heating gently, a violent reaction ensues; torrents of hydrocyanic acid escape and dichloracetic acid is formed:—

$$CCl_3.CH(OH)_2 + KCN = CHCl_2.CO.OH + HCN + KCl$$

Monobromacetic Acid $\left.\begin{matrix}CH_2Br.CO\\H\end{matrix}\right\}O$ is obtained by heating together bromine and acetic acid in sealed tubes to 150°. It forms colourless deliquescent crystals, melting below 100°, and boiling at 208°. Its salts are very unstable, and decompose readily into a metallic bromide and glycollic acid. *Ethyl monobromacetate* $\left.\begin{matrix}CH_2Br.CO\\C_2H_5\end{matrix}\right\}O$, a colourless liquid, possessing a very pungent smell, and attacking the mucous membranes and the eyes, is readily formed by heating the acid with ethyl alcohol. By heating this ether with potassium iodide, *ethyl moniodacetate* $\left.\begin{matrix}CH_2I.CO\\C_2H_5\end{matrix}\right\}O$ is formed, an oily liquid with a very irritating smell. This body is easily decomposed by baryta-water; by treating the barium salt thus obtained with sulphuric acid, *moniodacetic acid* is set free, which crystallizes in colourless, non-deliquescent plates. It melts at 82°, undergoing partial decomposition; on heating it stronger it is entirely destroyed, carbonization taking place. When this acid is heated with concentrated hydriodic acid, iodine is set free and acetic acid is formed:—

$$C_2H_3IO_2 + HI = C_2H_4O_2 + I_2$$

This reaction explains why it is not possible to substitute hydrogen directly by iodine in acetic acid.

Dibromacetic Acid $\left.\begin{matrix}CHBr_2.CO\\H\end{matrix}\right\}O$ is a colourless liquid, boiling at 225°, which is obtained by heating four molecules of bromine with one molecule of acetic acid. It can be easily transformed into *di-iodacetic acid*, which is sparingly soluble in water, and forms white crystals.

Tribromacetic Acid $\left.\begin{matrix}CBr_3.CO\\H\end{matrix}\right\}O$ crystallizes in shining tables, melting at 130° and boiling with partial decomposition at 245°. It is obtained by the action of nitric acid upon *bromal* C_2Br_3OH, a liquid resembling chloral, boiling at 172°, and produced by acting with dry bromine upon absolute alcohol.

Cyanacetic Acid $\left.\begin{matrix}CH_2(CN)CO\\H\end{matrix}\right\}O$.—To prepare this acid, ethyl monochloracetate is heated with an aqueous solution of potassium cyanide for some time; the liquid is then neutralized with sulphuric acid and evaporated. The residue is acidulated with dilute sulphuric acid and exhausted with ether. On evaporating this solution the crude acid is left behind; to purify it the lead salt is prepared by treating the acid with water and lead carbonate, and the repeatedly recrystallized salt decomposed with hydrogen sulphide. Cyanacetic acid forms yellowish crystals; its salts are readily soluble in water, with the exception of the mercuric and the silver salt.

Cyanacetic acid is a monobasic acid as well as nitrile; on heating it with an alkali, bibasic malonic acid is formed:—

$$CH_2\left\{\begin{matrix}CN\\CO.OH\end{matrix}\right. + 2H_2O = CH_2\left\{\begin{matrix}CO.OH\\CO.OH\end{matrix}\right. + NH$$

SUBSTITUTION-PRODUCTS OF ACETONITRILE.

The compounds to be described here have never been produced from acetonitrile; that they nevertheless are derivatives of this compound is shown by their reactions. The starting-points for these bodies are the so-called *fulminates*, compounds which are polymeric with the cyanates, and which are salts of the unknown *fulminic acid* or *nitro-acetonitrile* $CN.C(NO_2)H_2$.

Silver Fulminate $CN.C(NO_2)Ag_2$.—To prepare this body, one part of silver is dissolved in twenty parts of nitric acid (specific gravity 1·36); twenty-seven parts of spirits of wine (containing 86 per cent.) are added, and the mixture is heated until gentle ebullition begins, when again the same quantity of spirits of wine is added. On cooling, fulminating silver crystallizes out in white needles, sparingly soluble in cold, but more readily in hot water. It is a very dangerous body, on account of its highly explosive properties. In preparing it, or in working with it, great precaution has to be observed, as it easily decomposes, even in the moist state, with a most fearful detonation. The formation of this compound is explained by the following equation:—

$$C_2H_6O + 2AgNO_3 + N_2O_3 = C_2(NO_2)NAg_2 + 2HNO_3 + 2H_2O$$

The nitrogen trioxide necessary for this reaction is furnished by the action of nitric acid upon alcohol. Fulminating silver is consequently also produced if nitrogen trioxide be passed into an alcoholic solution of silver nitrate. When potassium chloride is added to a boiling solution of silver fulminate the double salt $C_2(NO_2)NAgK$ crystallizes on evaporating the filtrate; it forms silvery shining scales, and decomposes on the application of heat with a violent explosion. Nitric acid produces in a solution of this salt a white precipitate of acid silver fulminate $C_2(NO_2)NAgH$.

Mercuric Fulminate $CN.C(NO_2)Hg$ is prepared on the large scale by dissolving one part of mercury in twelve parts of pure nitric acid (specific gravity 1·36), and adding twelve parts of spirits of wine, when a violent reaction sets in, which is kept in check by adding gradually more alcohol. First, the liquid blackens by the separation of metallic mercury, which, however, soon disappears again. On cooling, the fulminating mercury separates as a crystalline powder. It is nearly insoluble in cold water; from a boiling solution it is obtained in white prismatic crystals. When kindled in the open air it burns away like gunpowder, but by percussion it is decomposed with a violent detonation; it is used for filling percussion-caps. On heating it with water and zinc or copper, zinc fulminate $C_2(NO_2)NZn$, or copper fulminate $C_2(NO_2)NCu$ are obtained, both crystalline and soluble salts.

Hydrogen sulphide decomposes the fulminates with the formation of a metallic sulphide, carbon dioxide, and ammonium sulphocyanate:—

$$CN.C(NO_2)Hg + 2H_2S = HgS + CO_2 + CN.SNH_4$$

Chlorine yields with fulminates a metallic chloride, cyanogen chloride, and chloropicrin:—

$$CN.C(NO_2)Hg + 3Cl_2 = HgCl_2 + CNCl + C(NO_2)Cl_3$$

Bromine decomposes a part of the mercury salt in a similar way, but there is also *dibromonitro-acetonitrile* $CN.C(NO_2)Br_2$ formed, large colourless crystals, possessing a most irritating smell, like chloropicrin.

Iodine, however, simply replaces the mercury, *di-iodonitro-acetonitrile* $CN.C(NO_2)I_2$ being formed, crystallizing from ether in large monoclinic prisms, melting with slight decomposition at 86°.

Fulminuric Acid $C_3H_3N_3O_3$.—This acid, formerly also called *isocyanuric acid*, is produced when mercuric fulminate is boiled with a concentrated solution of an alkaline chloride. By using potassium chloride, the solution yields on cooling a curdy precipitate, a compound of potassium fulminate with mercuric chloride, which is decomposed by hydrogen sulphide. The filtrate leaves on evaporation the potassium salt; on adding sugar of lead to its solution a white precipitate of lead fulminurate is obtained, which, when decomposed by hydrogen sulphide, yields the free acid. Fulminuric acid is a crystalline solid, very soluble in water and possessing a strongly acid taste. It is monobasic; its salts are mostly soluble, and crystallize well; on heating they decompose with a slight explosion. The constitution of this acid is not quite understood; its formation from a fulminate is explained by the following equation:—

$$2C_2(NO_2)NH_2 + H_2O = C_3(NO_2)N_2H_3O + NH_3 + CO_2$$

On introducing a fulminate gradually in small quantities into a mixture of concentrated sulphuric acid and nitric acid, *trinitroacetonitrile* $CN.C(NO_2)_3$, a crystalline mass, resembling camphor, is obtained, which is decomposed by water with the formation of ammonia, carbon dioxide, and nitroform (see page 102). The formation of trinitroacetonitrile is explained by the following equation:—

$$C_3(NO_2)N_2H_3O + 2NO_2.OH = CN.C(NO_2)_3 + CO_2 + NH_3 + H_2O$$

By acting with hydrogen sulphide on this compound, the ammonium salt of *dinitroacetonitrile* $CN.C(NO_2)_2H$ is formed:—

$$CN.C(NO_2)_3 + 4H_2S = CN.C(NO_2)_2NH_4 + 2H_2O + 4S$$

By adding an acid to the ammonium compound, dinitroacetonitrile separates out. It forms large colourless crystals, and is a monobasic acid, the hydrogen being easily replaced by metals. The silver salt is as explosive as silver fulminate.

PROPYL-GROUP.

Primary Propyl Alcohol $C_3H_7.OH$ occurs in small quantities in the fusel-oil of beetroot spirit, corn spirit, and cognac. To isolate it the fusel-oil is subjected to fractional distillation, and the portion boiling between 80° and 105° collected separately. This is a mixture of ethyl, propyl, and isobutyl alcohols, which cannot be separated by fractional distillation, as their boiling-points are too close together.

	Boiling-point.
Ethyl Alcohol	78°·4
Propyl Alcohol	97
Isobutyl Alcohol	108

The liquid is therefore acted upon by phosphorus and iodine or bromine, to obtain the iodides or bromides, the boiling-points of which differ much more, so that it is easy to obtain pure compounds by fractional distillations. The boiling-points of these compounds are:—

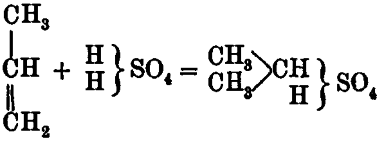
Ethyl Iodide	72°	Ethyl Bromide	39°
Propyl Iodide	102	Propyl Bromide	71
Isobutyl Iodide	121	Isobutyl Bromide	92

The bromide or iodide of propyl is next heated in sealed tubes with concentrated acetic acid and potassium acetate, and the propyl acetate thus formed is converted into the alcohol by heating it with a solution of potash. On distillation, aqueous propyl alcohol is obtained, which may be rendered anhydrous by a similar method to that by which absolute alcohol is obtained.

Propyl alcohol has also been obtained by synthesis from ethyl alcohol. It is a light colourless liquid, resembling common alcohol; on oxidation it yields *propionaldehyde* C_3H_6O, a liquid boiling at 50°, and *propionic acid.*

Propionic Acid $\left.\begin{matrix}C_3H_5O\\H\end{matrix}\right\}O$ is best prepared by boiling propionitrile with an alcoholic solution of caustic potash as long as ammonia is given off. The solution is then evaporated, and the residue distilled with diluted sulphuric acid. Propionic acid is a colourless liquid boiling at 140°, and having an acid smell. It mixes with water in all proportions, but by adding calcium chloride to the aqueous solution, the acid separates as a light oily layer. From this property its name has been derived, being the first member of the series showing the properties of a fat (*πρῶτον πῖον*). Amongst the salts, lead propionate $Pb(C_3H_5O_2)_2$ is most characteristic; it is very soluble in water, and does not crystallize, but dries up into an amorphous gum-like mass.

Secondary Propyl Alcohol, or Dimethyl Carbinol $\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\}CH.OH$, also called isopropyl alcohol, may be obtained from the primary alcohol by heating it with an excess of concentrated sulphuric acid, by which it is decomposed into water and *propene* C_3H_6. This gas is absorbed by shaking it with cold sulphuric acid, and *isopropyl sulphuric acid* is formed, thus:—

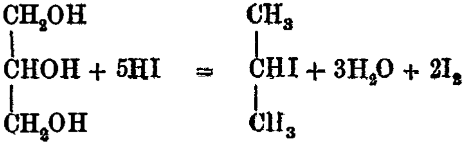


$$\begin{matrix}CH_3\\ | \\ CH\\ \| \\ CH_2\end{matrix} + \left.\begin{matrix}H\\H\end{matrix}\right\}SO_4 = \begin{matrix}CH_3\\CH_3\end{matrix}\!>\!\left.\begin{matrix}CH\\H\end{matrix}\right\}SO_4$$

which on boiling with water is decomposed into sulphuric acid and the secondary alcohol. To obtain it in larger quantity, it is best to act on its iodide with silver salts, and to decompose the ethers thus formed with caustic potash.

Dimsthyl carbinol is a colourless liquid with a vinous smell, boiling at 84°. It mixes with water in all proportions, and forms a hydrate $2C_3H_8O + H_2O$, which boils without decomposition at 78°, and has thus the same composition and boiling-point as ethyl alcohol. On heating it with the hydracids of the chlorine elements, the secondary chloride, bromide, and iodide are obtained.

Isopropyl Iodide $\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\}CHI$ is also formed by the direct combination of propene and hydriodic acid, but is best prepared by heating glycerin $C_3H_8O_3$, a triad alcohol, with an excess of fuming hydriodic acid:—

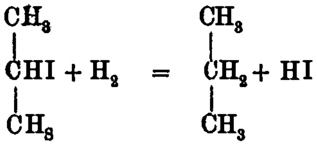


$$\begin{matrix}CH_2OH\\ | \\ CHOH\\ | \\ CH_2OH\end{matrix} + 5HI = \begin{matrix}CH_3\\ | \\ CHI\\ | \\ CH_3\end{matrix} + 3H_2O + 2I_2$$

It is a heavy colourless liquid, boiling at 89°. When it is heated with water and silver oxide, isopropyl alcohol and *isopropyl ether* $\left.\begin{matrix}(CH_3)_2CH\\(CH_3)_2CH\end{matrix}\right\}O$—a light mobile liquid with an ethereal smell and boiling at 60°—are formed.

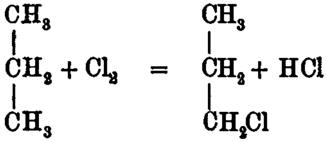
On bringing the iodide together with water and hydrochloric acid, *propane* C_3H_8 is evolved, a gas burning with a luminous flame. When acted upon by chlorine in diffused daylight, it yields, besides other substitution-products, primary propyl chloride. This transformation from the secondary to primary propyl compounds takes place according to the following equations:—

(1)



$$\begin{array}{l} \mathrm{CH_3} \\ | \\ \mathrm{CHI + H_2} \\ | \\ \mathrm{CH_3} \end{array} = \begin{array}{l} \mathrm{CH_3} \\ | \\ \mathrm{CH_2 + HI} \\ | \\ \mathrm{CH_3} \end{array}$$

(2)



$$\begin{array}{l} \mathrm{CH_3} \\ | \\ \mathrm{CH_2 + Cl_2} \\ | \\ \mathrm{CH_3} \end{array} = \begin{array}{l} \mathrm{CH_3} \\ | \\ \mathrm{CH_2 + HCl} \\ | \\ \mathrm{CH_2Cl} \end{array}$$

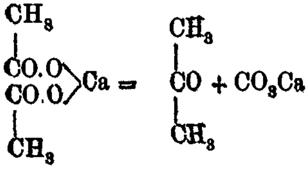
By this reaction, and those before described, we are therefore able to transform the primary propyl compounds into secondary ones, and *vice versâ*.

Cyanides of Isopropyl.—By heating isopropyl iodide with an alcoholic solution of potassium cyanide, isobutyronitrile $\left.\begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_3}\end{matrix}\right\}\mathrm{CH.CN}$ is formed, together with the isomeric *isopropylcarbamine* $\left.\begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_3}\end{matrix}\right\}\mathrm{CH.NC}$, which may be obtained in larger quantities by treating silver cyanide with isopropyl iodide. This compound boils at 87°, and has, like all carbamines, a most penetrating unpleasant smell; its vapour produces an unbearable bitter taste in the throat. When heated with aqueous hydrochloric acid for a few hours to 140°, it yields formic acid and *isopropylamine* $\left.\begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_3}\end{matrix}\right\}\mathrm{CH.NH_2}$, a mobile liquid having an ammoniacal and sweetish smell, and boiling at 32°.

Acetone, Dimethylketone $\left.\begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_3}\end{matrix}\right\}\mathrm{CO}$.—On adding a cold diluted solution of chromic acid to isopropyl alcohol, it is oxidized to acetone, which is also obtained by acting on zinc-methyl with acetyl chloride :—

$$2\mathrm{CO}\left\{\begin{matrix}\mathrm{Cl}\\ \mathrm{CH_3}\end{matrix}\right. + \mathrm{Zn}\left\{\begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_3}\end{matrix}\right. = \mathrm{ZnCl_2} + 2\mathrm{CO}\left\{\begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_3}\end{matrix}\right.$$

The best method, however, to obtain it in large quantities, is by the distillation of calcium acetate :—



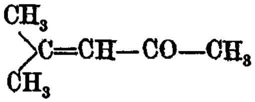
$$\begin{array}{l} \mathrm{CH_3} \\ | \\ \mathrm{CO.O} \\ \mathrm{CO.O} \\ | \\ \mathrm{CH_3} \end{array}\!\!\!>\mathrm{Ca} = \begin{array}{l} \mathrm{CH_3} \\ | \\ \mathrm{CO + CO_3Ca} \\ | \\ \mathrm{CH_3} \end{array}$$

It is also formed when the vapour of acetic acid is passed through a red-hot tube, and further, by the destructive distillation of sugar, tartaric acid, wood, &c., and is therefore contained in crude wood-spirit.

Acetone is a mobile liquid, boiling at 56°, and having a pleasant smell. It is miscible with water, and combines, like the aldehydes, with the acid sulphites of the alkali-metals, forming crystalline compounds, which are but sparingly soluble in water.

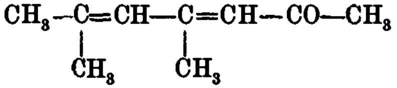
By the action of acids on acetone it loses the elements of water, and yields products of condensation.

Methyl-isobutenyl Ketone $C_6H_{10}O$, commonly called *mesityl oxide*, is obtained by gradually adding strong sulphuric acid to acetone, or if acetone is left standing over quicklime for some time, and afterwards distilled. It is a colourless oil, smelling like peppermint, and boiling at 130°. It has the following constitution:—



$$\begin{matrix} CH_3 \\ \end{matrix}\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\begin{matrix} \\ \end{matrix}{}^{CH_3}_{CH_3}\!\!>C{=}CH{-}CO{-}CH_3$$

Besides this substance another compound, called *acetophorone* $C_9H_{14}O$, is formed by the above reaction. It forms yellowish crystals, melting at 28°, and boiling at 196°. Its constitution is probably the following:—

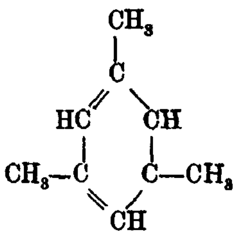


$$CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH{-}CO{-}CH_3$$

When acetone is heated with concentrated sulphuric acid, mesitylene C_9H_{12} is obtained:—

$$3C_3H_6O = C_9H_{12} + 3H_2O$$

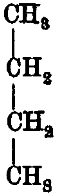
This hydrocarbon belongs to the group of aromatic compounds, and is trimethylbenzene:—



BUTYL-GROUP.

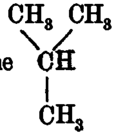
The compounds of the tetracarbon-series are derivatives of the following two paraffins :—

Butane



$CH_3-CH_2-CH_2-CH_3$

Trimethyl-methane



$(CH_3)_2CH-CH_3$

From butane, compounds of primary and secondary butyl are derived, and from trimethyl-methane primary and tertiary compounds.

DERIVATIVES OF BUTANE.

Butane or Diethyl C_4H_{10} is a colourless and very inflammable gas, burning with a luminous flame. By strong pressure or by cold it is condensed into a liquid, boiling at + 1°, and having the specific gravity 0·600 It is found in the most volatile portion of Pennsylvanian rock-oil, and in the distillation-products of cannel and boghead coal. To prepare it, ethyl iodide is heated in sealed tubes with the required quantity of clean zinc, and with its own volume of dry ether, for some hours to 100°, until all the metal has disappeared, half of the iodide being converted into zinc-ethyl. The tubes are now opened before the blow-pipe to allow the escape of any ethane which might have formed by the presence of traces of moisture, the tubes are sealed again, and heated during some hours to 130°—140°. After cooling them in ice-water the points are opened, and the butane driven out by gently heating, and collected in a gasholder.

When butane is mixed with an equal volume of chlorine and exposed to the light, substitution-products are formed, amongst which *butyl chloride* C_4H_9Cl is found.

Normal Butyl Alcohol $C_4H_9.OH$ is easily obtained in quantity by dissolving butyraldehyde in water, and gradually adding liquid sodium amalgam and an equivalent quantity of dilute sulphuric acid. On distilling the product, butyl alcohol passes over with the first portion of the distillate, and by repeating this operation a concentrated aqueous solution is obtained, from which on adding potassium carbonate, the alcohol separates out as a light layer. To remove the water still adhering, the liquid is first dried over fused potassium carbonate, and then over caustic baryta, or is repeatedly distilled over small quantities of sodium.

Normal butyl alcohol is a limpid, mobile liquid, having a vinous smell, and boiling at 116°.

Butyl Chloride C_4H_9Cl is prepared by saturating the alcohol with gaseous hydrochloric acid, and heating this solution together with some concentrated aqueous acid to 100° until the liquid has separated into two layers, the upper one of which consists of the chloride. It is a colourless liquid boiling at 77°·6.

Butyl Iodide C_4H_9I is best prepared by acting with iodine and phosphorus on the crude alcohol, and purifying the product by fractional distillation; it is a liquid boiling at 129°·6.

Butylamine $C_4H_9.NH_2$ is prepared by heating an alcoholic solution of butyl chloride with potassium cyanate in sealed tubes to 110°, and boiling the solution of butyl carbimide thus formed with caustic potash. It is a limpid liquid, boiling at 75°·5, and having great resemblance in all its properties to ethylamine.

The essential oil of the scurvy-grass (*Cochlearia officinalis*) contains *butyl sulphocarbimide* $\left.\begin{matrix}C_4H_9\\CS\end{matrix}\right\}N$, a liquid having a very pungent taste and smell, and boiling at 160°.

Butyric Acid $\left.\begin{matrix}C_4H_7O\\H\end{matrix}\right\}O$ occurs, together with other fatty acids, in butter, and is also found in the fruit of *Gingko biloba*, in human perspiration, in the flesh-juice, and the juice of different beetles. It is best prepared from sugar, which, if old cheese be added to its aqueous solution, undergoes fermentation by which it is first transformed into lactic acid, and afterwards into butyric acid. This fermentation only takes place if the solution remains neutral; chalk is therefore added to neutralize all the acid formed. The following proportions answer well:—3 kilograms of cane-sugar and 15 grams of tartaric acid are dissolved in 13 kilograms of boiling water; a few days afterwards 120 grams of old rotten cheese, which has been stirred up in 4 kilograms of sour milk, and 1½ kilogram of chalk are added. The mixture must be kept at a temperature of 30°—35° for some weeks. After about twenty days the liquid assumes a pasty consistence, calcium lactate crystallizing out, which soon disappears again, being converted into calcium butyrate with the simultaneous evolution of carbon dioxide and hydrogen:—

$$2C_3H_6O_3 = C_4H_8O_2 + 2CO_2 + 2H_2$$

When the fermentation is finished, a solution of 4 kilograms of crystallized sodium carbonate is added, the liquid is filtered, concentrated by evaporation, and decomposed by sulphuric acid. Butyric acid separates as an oily layer, which is dried over calcium chloride and rectified.

It is a colourless liquid, boiling at 162°, and possessing a penetrating sour smell, which in presence of ammonia becomes unpleasant, like perspiration. It is soluble in water, but separates again if soluble salts are added to this solution. Amongst the salts *calcium butyrate*

$\left.\begin{matrix}C_4H_7O_2\\C_4H_7O_2\end{matrix}\right\}$ Ca + H_2O is most characteristic, as it is more soluble in cold than in hot water, and thus on heating its cold saturated solution it separates in shining crystalline plates.

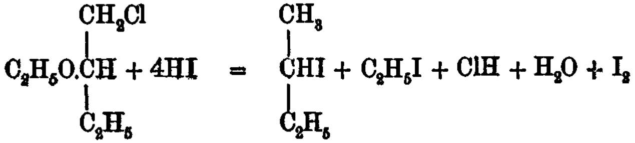
On heating an intimate mixture of butyrate and formate of calcium a distillate is obtained containing a large quantity of *butyraldehyde* $C_4H_{10}O$, a liquid boiling at about 75°.

Ethyl Butyrate $\left.\begin{matrix}C_4H_7O\\C_2H_5\end{matrix}\right\}$ O is obtained by distilling sodium butyrate with alcohol and sulphuric acid. It is a colourless liquid, boiling at 119°, and having a pleasant smell of fruit; it is used in the manufacture of artificial rum, &c. The same compound is formed by the action of ethyl iodide upon sodacetic ether (see page 140).

Secondary Butyl Alcohol, or Ethyl-methyl Carbinol $\left.\begin{matrix}C_2H_5\\CH_3\end{matrix}\right\}$ CH OH.—The iodide of this alcohol is obtained by heating erythrite $C_4H_{10}O_4$, a tetrad alcohol, with concentrated hydriodic acid, just as triad glycerine yields under the same circumstances dimethyl carbinol:—

$$C_4H_{10}O_4 + 7IH = C_4H_9I + 4H_2O + 3I_2$$

The same iodide is formed when ethylated monochlorethyl oxide (see page 111) is heated in sealed tubes with concentrated hydriodic acid:—



$$\begin{array}{lcl}CH_2Cl & & CH_3\\ | & & |\\ C_2H_5O.CH + 4HI & = & CHI + C_2H_5I + ClH + H_2O + I_2\\ | & & |\\ C_2H_5 & & C_2H_5\end{array}$$

Secondary butyl iodide boils at 119°. On heating it with concentrated acetic acid and silver acetate a portion of it decomposes into hydriodic acid and butene, and another yields secondary butyl acetate:—

$$(1)\quad C_4H_9I + \left.\begin{matrix}C_2H_3O\\Ag\end{matrix}\right\}O = C_4H_8 + AgI + \left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O$$

$$(2)\quad C_4H_9I + \left.\begin{matrix}C_2H_3O\\Ag\end{matrix}\right\}O = \left.\begin{matrix}C_4H_9\\C_2H_3O\end{matrix}\right\}O + AgI$$

Secondary butyl acetate has a pleasant smell of fruit, and boils at 111°. On heating it with caustic potash it yields ethyl-methyl carbinol, a liquid boiling at 99°, having a vinous smell. When it is treated with a solution of potassium dichromate in cold dilute sulphuric acid, it is oxidized to *ethyl-methyl ketone* $\left.\begin{matrix}C_2H_5\\CH_3\end{matrix}\right\}$ CO, a liquid resembling common acetone, and boiling at 81°. The same compound is formed by the action of acetyl chloride upon zinc-ethyl:—

$$2\left.\begin{matrix}Cl\\CH_3\end{matrix}\right\}CO + \left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}Zn = ZnCl_2 + 2\left.\begin{matrix}C_2H_5\\CH_3\end{matrix}\right\}CO$$

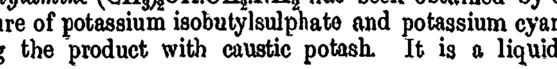
DERIVATIVES OF TRIMETHYL-METHANE.

Isobutyl Alcohol $\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\}CH.CH_2.OH$ occurs in the same fusel-oil in which propyl alcohol is found, and is present in a larger quantity. To obtain it pure, that portion which after repeated fractional distillation boils between 105° and 115° is by means of phosphorus and iodine converted into the iodide, which by repeated distillation is freed from the iodides of propyl and amyl.

Isobutyl iodide boils at 121°. By converting it into the acetate and heating this ether with caustic potash, pure isobutyl alcohol is obtained as a colourless liquid, which refracts light strongly and smells like fusel-oil; it boils at 108°.

Isobutyric Acid $\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\}CH.CO.OH$ is obtained by oxidizing isobutyl alcohol, and exists in carob, the fruit of *Ceratonia siliqua*; it boils at 153°, and smells like common butyric acid, but less unpleasant. From the latter acid it not only differs by its lower boiling-point, but also by the properties of its salts. *Calcium isobutyrate* $(C_4H_7O_2)Ca + 3H_2O$ crystallizes in prisms which are much more soluble in hot than in cold water.

Isobutyric acid has also been prepared synthetically in two ways. Its nitrile is obtained by heating potassium cyanide with isopropyl iodide, and on boiling this nitrile with caustic potash isobutyric acid is formed:—



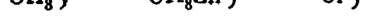
$$\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\}CH.CN + 2H_2O = \left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\}CH.CO.OH + NH_3$$

Ethyl isobutyrate is formed by acting with methyl iodide upon disodacetic ether:—

$$Na_2CH.CO.OC_2H_5 + 2CH_3I = (CH_3)_2CH.CO.C_2H_5 + 2NaI$$

Isobutylamine $(CH_3)_2CH.CH_2.NH_2$ has been obtained by distilling a mixture of potassium isobutylsulphate and potassium cyanate, and treating the product with caustic potash. It is a liquid boiling at 67°.

Tertiary Butyl Alcohol, or Trimethyl Carbinol $\left.\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\right\}COH$.—When one molecule of zinc-methyl is added gradually to two molecules of acetyl chloride, dimethyl ketone is formed; but on adding *two* molecules of zinc methyl to one of acetyl chloride, the liquid becomes converted after a few days into white crystals, which are formed by the addition of zinc-methyl to acetone, in a similar manner to that in which acetone combines with one molecule of hydrogen:—



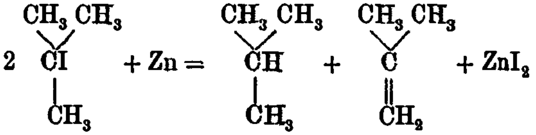
$$CH_3.COCl + 2\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\}Zn = \left.\begin{matrix}(CH_3)_3C\\CH_3Zn\end{matrix}\right\}O + \left.\begin{matrix}CH_3\\Cl\end{matrix}\right\}Zn$$

The same crystalline compound is obtained by the action of carbonyl chloride upon zinc-methyl. By water it is decomposed, marsh-gas is evolved, and trimethyl carbinol is formed, the monad group $ZnCH_3$ being replaced by hydrogen :—

$$\left.\begin{matrix}(CH_3)_3C\\ CH_3Zn\end{matrix}\right\}O + 2H_2O = \left.\begin{matrix}(CH_3)_3C\\ H\end{matrix}\right\}O + CH_4 + Zn(OH)_2$$

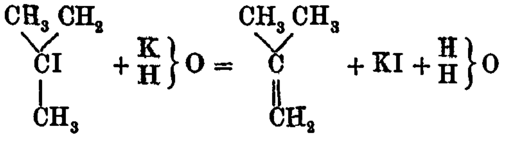
In order to isolate the alcohol the liquid is distilled, and to the distillate potassium carbonate is added, by which the alcohol separates as a light layer, which must be dried over calcium chloride and rectified. If quite anhydrous it forms colourless crystals ; it melts at 25°, and boils at 82°·5 ; its smell reminds one at the same time of alcohol and of camphor. By passing hydriodic acid gas into well-cooled trimethyl carbinol, tertiary butyl iodide $(CH_3)_2CH.CH_2I$ is obtained, a heavy colourless liquid boiling at 99°, which in contact with moist silver oxide is again transformed into the alcohol. If the iodide is acted upon by silver acetate and acetic acid, the acetate of tertiary butyl is obtained, a colourless liquid which smells like acetic acid and peppermint, and boils at 96°.

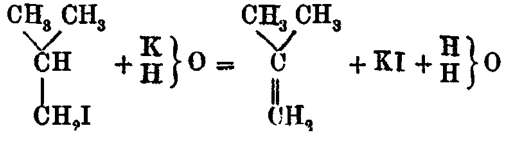
In presence of zinc and water the iodide is converted into *trimethyl-methane* $CH(CH_3)_3$, and *isobutene* C_4H_8 :—



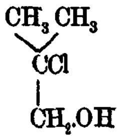
To separate the two gases they are passed through bromine, which combines with the isobutene, whilst the trimethyl-methane passes through unabsorbed. Trimethyl-methane is condensed by a freezing mixture into a mobile liquid, boiling at – 17°. When this hydrocarbon is acted upon by chlorine it is converted again into tertiary butyl chloride, which is also formed by the action of iodine chloride upon isobutyl iodide.

Isobutene has also been produced by heating tertiary butyl iodide or primary isobutyl iodide with an alcoholic solution of potash :—

(1) 

(2) 

With hydriodic acid isobutene readily combines, forming again tertiary butyl iodide; it can also be easily transformed into the tertiary alcohol by dissolving it in dilute sulphuric acid and distilling. By means of this reaction, large quantities of the tertiary alcohol may be obtained from isobutyl alcohol. When isobutene is shaken with aqueous hypochlorous acid the gas is absorbed, and *isobutene chlorhydrate* is formed, which has the following constitution:—



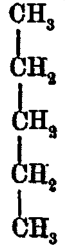
On adding sodium amalgam to its aqueous solution the chlorine is replaced by hydrogen, and isobutyl alcohol is formed.

Trimethylcarbinylamine or Tertiary Butylamine $C(CH_3)_3NH_2$.—When isobutyl iodide is heated with dry silver cyanate, a dry, solid compound of silver iodide and butyl carbimide is formed; this, mixed with finely divided caustic potash and heated, gives off vapours of trimethylcarbinylamine, a colourless liquid, boiling at 45°.

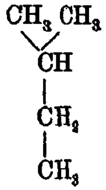
AMYL OR PENTYL-GROUP.

Theory points out the existence of three isomeric hydrocarbons C_5H_{12}:—

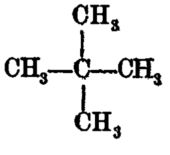
Pentane.



Dimethyl-ethylmethane.



Tetramethyl-methane.



(1) DERIVATIVES OF PENTANE.

Pentane C_5H_{12} is a colourless mobile liquid having an ethereal smell, and boiling at 39°. It occurs in the light oils obtained by the distillation of boghead and cannel coal, and in American petroleum. On passing chlorine into its vapour a mixture of a primary and a secondary chloride is obtained, from which by a reaction already described primary pentyl alcohol and methyl-propyl carbinol can be prepared.

Primary Pentyl Alcohol $\left.\begin{matrix}C_5H_{11}\\H\end{matrix}\right\}O$ has also been obtained from pentylic acid by the same reaction by which butyric acid is transformed into butyl alcohol; it is a liquid boiling at 137°, and smelling like fusel-oil.

Pentylic Acid $\left.\begin{matrix}C_5H_9O\\H\end{matrix}\right\}O$, also called *normal valerianic acid*, has been obtained by heating butyl iodide with potassium cyanide, and boiling the *pentonitrile* $C_4H_9.CN$ thus formed with an alcoholic solution of caustic potash. It is a colourless liquid which boils at 186°.

Methyl-propyl Carbinol $\left.\begin{matrix}CH_3\\C_3H_7\end{matrix}\right\}CH.OH$ is a liquid boiling at 120°. The iodide of this secondary alcohol is formed by combining hydriodic acid with *pentylene* or *isamylene* C_5H_{10}, a hydrocarbon which will be mentioned under dyad radicals. The *secondary pentyl iodide* boils at 146°; by acting on it with silver acetate, the acetic ether of the alcohol is formed, from which by means of caustic potash the alcohol itself is easily obtained.

On oxidizing it with a dilute solution of potassium permanganate it yields *methyl-propyl ketone* $\left.\begin{matrix}CH_3\\C_3H_7\end{matrix}\right\}CO$, which has also been prepared by distilling a mixture of calcium butyrate and sodium acetate. It is a liquid having a fragrant smell, and boiling at 103°.

(2) DERIVATIVES OF DIMETHYL-ETHYLMETHANE.

The compounds which belong to this group have been known for a long time, and are well investigated. The starting-point for them is the *primary amyl alcohol* $CH\left\{\begin{matrix}(CH_3)_2\\C_2H_4.OH\end{matrix}\right.$, which occurs in most fusel-oils, and forms the chief portion of those from corn and potato spirit. Its name is derived from this circumstance, *amylum* being the Latin name for starch

It can easily be isolated by fractional distillation, and is a colourless, somewhat oily liquid, which boils at 132°, and possesses a penetrating unpleasant smell. At − 20° it solidifies into a crystalline mass. Amyl alcohol turns the plane of the polarized light to the left, but the rotating power of different samples varies very much; the cause of this is, that common amyl alcohol is a mixture of an optically active and an inactive alcohol, in which generally the latter preponderates.

These two modifications can be separated by dissolving the alcohol in concentrated sulphuric acid, and preparing from this solution the two barium amylsulphates, which are separated by repeated recrystallization, that derived from the inactive alcohol being much more soluble in water than the other. To reconvert these two salts into the alcohols, they are first transformed into the sodium salts, and then distilled with dilute sulphuric acid.

The two amyl alcohols differ, not only by their physical, but also by their chemical properties. Thus whilst the inactive alcohol yields on oxidation only valerianic acid, the active one also gives some acetic acid and carbon dioxide.

Amyl Chloride $C_5H_{11}Cl$, a colourless liquid boiling at 102°, has been prepared by heating amyl alcohol with hydrochloric acid.

Amyl Bromide $C_5H_{11}Br$ is best prepared by acting upon amyl alcohol with phosphorus and bromine; it boils at 121°. *Amyl iodide* $C_5H_{11}I$ is obtained in a similar way by using iodine instead of bromine; it is a heavy liquid which boils at 147°.

If amyl iodide is brought in contact with hydrochloric acid and zinc, or if it is heated in sealed tubes with water and zinc to 150°, *dimethyl-ethylmethane* $CH\left\{\begin{matrix}(CH_3)_2\\ C_2H_5\end{matrix}\right.$, commonly called *amyl hydride*, is formed, a liquid resembling pentane, and boiling at 30°.

Amyl Oxide $\left.\begin{matrix}C_5H_{11}\\ C_5H_{11}\end{matrix}\right\}O$ or *diamyl ether* is prepared either by heating amyl alcohol with sulphuric acid or by acting on sodium amylate with amyl iodide. It is also formed by heating ten parts of amyl alcohol and one part of amyl iodide in sealed tubes to 200°. In the latter reaction amyl ether and hydriodic acid are formed, the latter acting on the excess of amyl alcohol to form amyl iodide again. Thus with a small quantity of the iodide a large quantity of the alcohol may be converted into the ether, but the reaction comes to an end after some time, the hydriodic acid becoming so dilute that its action ceases.

Ethyl-amyl Ether $\left.\begin{matrix}C_2H_5\\ C_5H_{11}\end{matrix}\right\}O$.—This compound can be prepared by a great number of reactions. It is formed by heating amyl chloride or iodide with sodium ethylate, or an alcoholic solution of caustic potash; or by acting with ethyl iodide upon sodium amylate; or by either running ethyl alcohol into a heated mixture of concentrated sulphuric acid and amyl alcohol, or by the converse process of adding amyl alcohol to a mixture of sulphuric acid and ethyl alcohol. It boils at 112°.

Amyl Nitrite $C_5H_{11}NO_2$ is prepared by passing nitrogen trioxide into amyl alcohol. It is a colourless liquid which boils at 99°, and possesses in the highest degree that peculiar choking smell which most amyl compounds exhibit; its vapour, if inhaled even in small quantity, produces palpitation of the heart, and determination of the blood to the head.

Amyl Nitrate $C_5H_{11}NO_3$.—To prepare this ether, to a mixture of one volume of common strong nitric acid and three volumes of concentrated nitric acid, which is surrounded by a mixture of ice and salt, one volume of amyl alcohol is gradually added, the liquid being constantly stirred up. The amyl nitrate separates as a light oily layer; it boils at 148°, and smells like bugs. The inhaling of its vapour produces headache and choking.

Amyl Acetate $\left.\begin{matrix}C_5H_{11}\\C_2H_3O\end{matrix}\right\}O$ is prepared by distilling sodium acetate with a mixture of amyl alcohol and sulphuric acid. It is a colourless liquid, which boils at 140°, and smells like jargonelle pears. It is used by confectioners and perfumers under the name of "pear oil."

Amylamine $C_5H_{11}.NH_2$ is a colourless liquid, which boils at 95°, has an ammoniacal smell, and is very caustic. It is soluble in water; the solution has a strong alkaline reaction, and gives with metallic salts the same reactions as ethylamine.

On adding it to a solution of chloroform and caustic potash in alcohol, *amyl carbamine* $C_5H_{11}.NC$ is formed, a liquid which boils at 137°, and has a bitter taste and an intolerable smell. This compound is also obtained by the action of silver cyanide upon amyl chloride together with its isomeride *isocapronitrile* $C_5H_{11}.CN$, which, however, is best prepared by distilling a mixture of potassium amylsulphate with potassium cyanide. Isocapronitrile boils at 146°, and has an ethereal penetrating smell. On heating it with caustic potash solution it yields isocaproic acid.

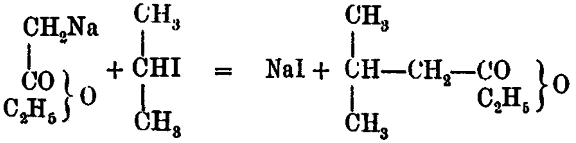
Valeraldehyde $C_5H_{10}O$.—To prepare this compound a mixture of one part of amyl alcohol and four parts of concentrated sulphuric acid is run slowly into a retort containing four parts of water and five parts of potassium dichromate. By the violent reaction which ensues sufficient heat is evolved to volatilize the aldehyde. To obtain it quite pure, it is shaken with a concentrated solution of acid sodium sulphite, to obtain the compound $2C_5H_{10}\left\{\begin{matrix}OH\\SO_3Na\end{matrix}\right. + H_2O$, which is pressed between blotting paper and recrystallized from hot water. On distilling this compound with a dilute solution of caustic soda, we obtain pure valeraldehyde, a liquid possessing a suffocating odour, and boiling at 92°·5.

It combines with nascent hydrogen, amyl alcohol again being formed.

Valerianic Acid $\left.\begin{matrix}C_5H_9O\\H\end{matrix}\right\}O$ occurs in the roots of the common valerian (*Valeriana officinalis*), and of *Angelica Archangelica*, in the bark and berries of the wild guelder rose (*Viburnum opulus*), and in the train-oil of *Delphinus globiceps*.

From valerian root it may be obtained by distilling the root with water; it is, however, best prepared by oxidizing amyl alcohol, using the same proportions as in the preparation of its aldehyde, but connecting the vessel with a reversed condenser, to allow the aldehyde to flow back, and come again in contact with the oxidizing mixture. When the reaction has ceased, the liquid is distilled, and the distillate neutralized with sodium carbonate, when some amyl valerate which has formed at the same time remains undissolved. The solution of the sodium salt is evaporated, and the residue decomposed by dilute sulphuric acid. The acid, which separates out as a light oily layer, is dried over calcium chloride and rectified. Valerianic acid is a thin oily liquid, possessing a sour smell of rotten cheese, and boiling at 175°. It combines with water, forming a hydrate $C_5H_{10}O_2 + H_2O$, which boils without decomposition.

This acid has also been prepared by synthesis, and is formed by heating secondary propyl iodide with sodacetic ether:—



$$\left.\begin{array}{l}CH_2Na\\ |\\ CO\\ C_2H_5\end{array}\right\}O + \begin{array}{l}CH_3\\ |\\ CHI\\ |\\ CH_3\end{array} = NaI + \begin{array}{l}CH_3\\ |\\ CH-CH_2-CO\\ |\\ CH_3\end{array}\left.\begin{array}{r}\\ \\ \\ C_2H_5\end{array}\right\}O$$

Ethyl valerate is thus obtained, which is easily decomposed by alkalis.

Another synthesis consists in distilling sodium isobutylsulphate with potassium cyanide, by which reaction valeronitrile C_5H_9N is formed, which, on heating with caustic potash, yields potassium valerate. Most of the salts of valerianic acid are soluble in water, in the dry state they are odourless, but in the moist state they smell of the acid.

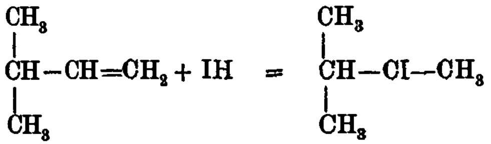
Zinc Valerate $(C_5H_9O_2)_2Zn$ forms scaly crystals, and is not very readily soluble in water, but dissolves easily in alcohol: it is used in medicine.

Silver Valerate $C_5H_9O_2Ag$ is a white precipitate, which can be re-crystallized from boiling water.

Amyl Valerate $\left.\begin{array}{l}C_5H_9O\\ C_5H_{11}\end{array}\right\}O$ is obtained, besides valerianic acid, by the oxidation of amyl alcohol. It is a liquid, boiling at 188°, and possessing an odour like apples. It is used by confectioners, and called "apple oil,"

The amyl alcohol possessing rotating power yields on oxidation, besides some carbon dioxide and acetic acid, a valerianic acid, which differs from that just described in different ways. It is optically active, turning the plane of polarized light to the right, whilst the alcohol turns it to the left. The same acid is formed by the putrefaction of albuminous substances, and is therefore found in old cheese. It boils at 170°, and forms salts which have the same composition and properties as those of the inactive acid, with the exception of the barium salt, which does not crystallize, but dries up to an amorphous mass, whilst that of the inactive acid crystallizes easily in large plates.

Secondary Amyl Alcohol $\left.\begin{array}{l}(CH_3)_2CH\\ CH_3\end{array}\right\}CH.OH$, *or Methyl-isopropyl Carbinol.*—When amyl alcohol is heated with zinc chloride, water and *amylene* C_5H_{10} are formed. This hydrocarbon combines with fuming hydriodic acid, and yields *secondary amyl iodide* :—



$$\begin{array}{l}CH_3\\ |\\ CH-CH=CH_2+IH\\ |\\ CH_3\end{array} = \begin{array}{l}CH_3\\ |\\ CH-CI-CH_3\\ |\\ CH_3\end{array}$$

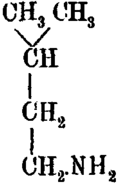
This iodide boils at 130°; by acting on it with silver salts a portion splits up into amylene and hydriodic acid, whilst another portion yields compound ethers.

The acetate, which boils at 125°, possesses an ethereal smell, quite different from that of the primary acetate.

When the iodide is acted on by silver oxide and water, besides a little amylene, the secondary alcohol is obtained, boiling at 108° and possessing a smell quite different from that of fusel-oil. It is sometimes called *amylene hydrate*, from the fact that on heating it to 200° it splits up into water and amylene.

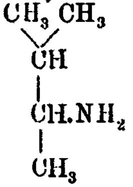
By the action of silver cyanide upon the secondary iodide, the corresponding carbimide is formed, which when distilled with an alkali yields *isamylamine*, which is isomeric with amylamine:—

Amylamine.



$$\begin{array}{l}CH_3\ CH_3\\ \quad \diagdown\diagup\\ \quad CH\\ \quad |\\ \quad CH_2\\ \quad |\\ \quad CH_2.NH_2\end{array}$$

Isamylamine.



$$\begin{array}{l}CH_3\ CH_3\\ \quad \diagdown\diagup\\ \quad CH\\ \quad |\\ \quad CH.NH_2\\ \quad |\\ \quad CH_3\end{array}$$

Isamylamine boils at 78·5°, and has an ammoniacal smell; it is soluble in water, and is as strong a base as amylamine.

Ethyldimethyl Carbinol $\left.\begin{matrix}(CH_3)_2\\ C_2H_5\end{matrix}\right\}COH$.—This tertiary amyl alcohol has been obtained from zinc-methyl and propionyl chloride. It is a thick liquid, boiling at 100°, and yielding on oxidation only acetic acid.

TETRAMETHYL-METHANE $C(CH_3)_4$

is formed by acting with zinc-methyl upon tertiary butyl iodide:—

$$2C(CH_3)_3I + Zn(CH_3)_2 = 2C(CH_3)_4 + ZnI_2$$

It has also been prepared by the action of zinc-methyl upon propidene dichloride $(CH_3)_2CCl_2$, a compound which is obtained by treating acetone $(CH_3)_2CO$ with phosphorus pentachloride. It boils at 9°·5, and solidifies at − 20° to a white mass.

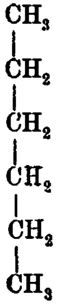
Tertiary Valerianic Acid $C(CH_3)_3CO_2H$, *or Trimethylacetic Acid.*—

This acid has been obtained by treating tertiary butyl iodide with mercuric cyanide, and decomposing the nitrile thus formed with alcoholic potash. The pure acid boils at 161°, and solidifies on cooling to a glassy mass mixed with crystals, melting at 35°. It has a pungent acid taste, and a faint sour smell. The corresponding alcohol is not known.

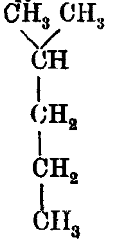
HEXYL GROUP.

Four paraffins having the formula C_6H_{14} are known:—

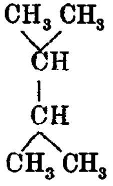
Hexane.



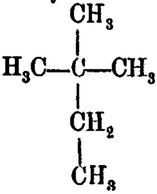
Dimethylpropylmethane.



Tetramethylethane.



Trimethylethylmethane.



(1) DERIVATIVES OF HEXANE.

Hexane, or Hexyl Hydride.—This hydrocarbon occurs in the light oils obtained in the destructive distillation of boghead and cannel coal, and in large quantities in Pennsylvania petroleum. Pure hexane is also formed by acting upon propyl iodide with sodium, or by treating the secondary hexyl iodide with zinc and hydrochloric acid. By passing dry chlorine gas into the vapour of boiling hexane a mixture of primary and secondary propyl chloride is formed, from which, by heating with glacial acetic acid and potassium acetate, the acetic ethers are obtained. On treating these acetates with an alcoholic solution of caustic potash the alcohols are formed, which cannot be completely separated by fractional distillation, as the difference between their boiling-points is only 15°.

Primary Hexyl Alcohol $\left.\begin{matrix}C_6H_{13}\\H\end{matrix}\right\}O$.—The essential oil of *Heracleum giganteum* consists chiefly of a mixture of hexyl butyrate and octyl acetate. By saponifying these ethers with caustic potash the alcohols are set free, and can easily be separated by distillation. Hexyl alcohol boils at 157°, and possesses a pleasant aromatic odour. *Hexyl iodide* $C_6H_{13}I$ is a heavy, colourless liquid, boiling at 179°·5. The acetate $\left.\begin{matrix}C_6H_{13}\\C_2H_3O\end{matrix}\right\}$ possesses a pleasant smell like fruit; it boils at 169°.

Normal Hexylic or Caproic Acid $\left.\begin{matrix}C_6H_{11}O\\H\end{matrix}\right\}O$ is obtained by oxidizing the alcohol, and has also been obtained from its nitrile or butyl cyanide. It is an oily liquid, possessing a pungent and sudorific smell, and boiling at 205°. It occurs in plants, as in *Satyrium hircinum* and in the fruit of *Gingko biloba.* Cocoa-nut oil, as well as butter, contain caproic acid besides caprylic and capric acids.[1] Caproic acid has also been found in human perspiration and in crude butyric acid obtained by fermentation.

To obtain the three acids from cocoa-nut oil, it is saponified with caustic soda and the soap distilled with dilute sulphuric acid; the volatile acids distil over, whilst non volatile fatty acids remain behind.

Secondary Hexyl Alcohol, or Methyl-butyl Carbinol $\left.\begin{matrix}CH_3\\C_4H_9\end{matrix}\right\}CH.OH$.— The iodide of this alcohol is formed by heating mannite $C_6H_8(OH)_6$ with an excess of fuming hydriodic acid:—

$$C_6H_8(OH)_6 + 11HI = C_6H_{13}I + 6H_2O + 5I_2$$

In preparing it amorphous phosphorus is added to the mixture, by means of which the free iodine is re-converted into hydriodic acid. The iodide boils at 165·5°; when it is treated with silver oxide and water it yields the alcohol besides *hexene* C_6H_{12} and *secondary hexyl ether*:—

$$(1) \quad C_6H_{13}I + AgOH = C_6H_{14}O + AgI$$

$$(2) \quad C_6H_{13}I + AgOH = C_6H_{12} + AgI + H_2O$$

$$(3) \quad 2C_6H_{13}I + 2AgOH = \left.\begin{matrix}C_6H_{13}\\C_6H_{13}\end{matrix}\right\}O + 2AgI + H_2O$$

Methyl-butyl carbinol boils at 137°, and yields on oxidation—

Methyl-butyl Ketone $\left.\begin{matrix}CH_3\\C_4H_9\end{matrix}\right\}CO$, a mobile liquid, boiling at 127°, which by further oxidation splits up into acetic acid and butyric acid· the same products are obtained by oxidizing the alcohol prepared from hexane.

(2) DERIVATIVES OF DIMETHYL-PROPYLMETHANE.

Dimethyl-propylmethane $CH\left\{\begin{matrix}CH_3\\CH_3\\C_3H_7\end{matrix}\right.$ is obtained by the action of sodium upon a mixture of ethyl iodide and isobutyl iodide, and has therefore been called ethyl-isobutyl. It boils at 62°. No derivatives have been obtained directly from this hydrocarbon, but there exists a hexyl alcohol in the fusel-oil from the marc of grapes, which most probably has a similar constitution as amyl alcohol, and appears to be a derivative of dimethyl-propylmethane. This isohexyl alcohol boils at 151°.

---

[1] The names of these three acids are derived from *capra* the goat, as they were first found in butter from goat's milk, and also because they possess the peculiar smell of the goat.

By acting with caustic potash on isocapronitrile (amyl cyanide) *isocaproic acid* $(CH_3)_2C_3H_5.CO_2H$ is formed, which for a long time was believed to be identical with the normal caproic acid; it has similar properties, but boils at 199°.

Dimethyl-propyl Carbinol $\left.\begin{matrix}CH_3\\CH_3\\C_3H_7\end{matrix}\right\}COH$.—This tertiary alcohol is formed by the action of zinc methyl upon butyryl chloride; it is a thick colourless liquid, boiling at 115°. Another tertiary hexyl alcohol, *methyl-diethyl carbinol* $\left.\begin{matrix}CH_3\\(C_2H_5)_2\end{matrix}\right\}COH$, resembling the latter, and boiling at 120°, has been prepared from zinc ethyl and acetyl chloride.

(3) DERIVATIVES OF TETRAMETHYL-ETHANE.

Tetramethyl-ethane or Di-isopropyl $C_2H_2(CH_3)_4$ is formed by acting with sodium upon secondary propyl iodide in presence of ether. It boils at 58°; its derivatives have been so far little studied.

Dimethyl-isopropyl Carbinol $\left.\begin{matrix}(CH_3)_2\\(CH_3)_2CH\end{matrix}\right\}COH$ is prepared by acting with zinc-methyl on isobutyryl chloride. It is a liquid boiling at 112° and solidifying at − 35° to slender silky needles. Like other tertiary alcohols it smells like camphor; chromic acid solution oxidizes it to dimethyl ketone.

Methylisopropyl-acetic Acid $\left.\begin{matrix}CH_3\\(CH_3)_2CH\end{matrix}\right\}CH.CO_2H$.—The nitrile of this acid has been produced by heating secondary amyl iodide with potassium cyanide. The free acid does not smell so unpleasantly as the other caproic acids, from which it also differs by the solubility and crystalline form of its salts.

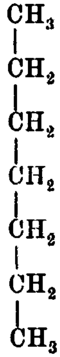
A fourth isomeric caproic acid, *diethyl-acetic acid* $(C_2H_5)_2CH.CO.OH$, is formed by acting with ethyl iodide upon disodacetic ether; this acid must be considered as a derivative of the same unknown hydrocarbon from which methyl-diethyl carbinol is theoretically derived.

Trimethyl-ethylmethane $C\left\{\begin{matrix}(CH_3)_3\\C_2H_5\end{matrix}\right.$ has been obtained by acting with zinc-ethyl on tertiary butyl iodide as a liquid boiling between 43° and 48°.

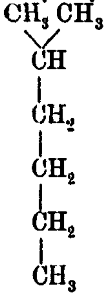
HEPTYL GROUP.

We know four isomeric hydrocarbons of the formula C_7H_{16}, viz.:—

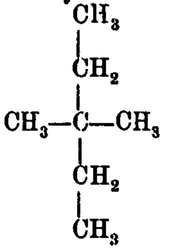
Heptane.



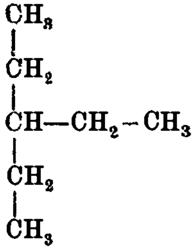
Dimethyl-butylmethane or Ethyl-amyl.



Dimethyl-diethylmethane.



Triethyl-methane.



Heptane occurs in Pennsylvania petroleum and in the coal tars containing other paraffins. Pure heptane is also obtained by distilling azelaïc acid $C_7H_{14}\left\{\begin{matrix}CO_2H\\CO_2H\end{matrix}\right.$ with caustic baryta; it boils at 100°·5. Ethyl-amyl is formed by acting on a mixture of the bromides or iodides of ethyl and amyl with sodium; it boils at 91°. The third of these paraffins has been prepared by the action of zinc-ethyl upon propidene dichloride $(CH_3)_2CCl_2$ (see tetramethyl-methane); it boils at 86°. Triethyl-methane is produced by the action of zinc-ethyl and sodium on ethyl orthoformate (see page 118); it boils at 96°.

By acting on these paraffins with chlorine different heptyl chlorides are produced, from which alcohols and other derivatives have been obtained. Thus heptane yields a primary heptyl alcohol boiling at about 175°, and a secondary boiling at 160°.

Œnanthyl Aldehyde or Œnanthol $C_7H_{14}O$ is formed by oxidizing primary heptyl alcohol, and may be obtained in quantity by subjecting castor-oil to destructive distillation. It is a colourless liquid, having a pungent smell and boiling at 154°; like other aldehydes it forms crystalline compounds with the acid sulphites of the alkali-metals.

Œnanthylic Acid $\left.\begin{matrix}C_7H_{13}O\\H\end{matrix}\right\}O$, or *heptylic acid*, is prepared by oxidizing œnanthol with dilute chromic acid. It is an oily liquid, having a faint, sour smell, and boiling at 223°. An isomeric acid has been obtained by treating sodacetic ether with amyl iodide.

Methyl-pentyl Ketone $\left.\begin{matrix}CH_3\\C_5H_{11}\end{matrix}\right\}CO$ is formed by the oxidation of secondary heptyl alcohol; it boils at 132° and yields on further oxidation acetic acid and pentylic acid.

Isoheptyl Alcohol $(CH_3)_2C_5H_9.OH$ has been obtained, together with *methyl-amyl carbinol* $\left.\begin{matrix}CH_3\\(CH_3)_2C_3H_5\end{matrix}\right\}CH.OH$, from ethyl-amyl. The primary alcohol boils at 165°, and yields on oxidation *isoheptylic acid* $(CH_3)_2C_4H_7.CO_2H$, an oily liquid boiling at 212°. The secondary alcohol boils at 146°.

Methyl-amyl Ketone $\left.\begin{matrix}CH_3\\(CH_3)_2C_3H_5\end{matrix}\right\}CO$ is a limpid liquid boiling at 144°, which has been produced by the action of zinc-methyl on isocaproyl chloride, as well as that of zinc-amyl on acetyl chloride, and is also formed by oxidizing methyl-amyl carbinol.

Triethyl Carbinol $C(C_2H_5)_3OH$.—This tertiary heptyl alcohol is produced by the action of zinc-ethyl on propionyl chloride. It is a colourless liquid, boiling at 142° and smelling like camphor. Chromic acid solution oxidizes it to *methyl-diethyl-ethene* $(C_2H_5)_2C = C.CH_3$, which by further oxidation is resolved into acetic acid and propionic acid.

OCTYL GROUP.

Normal Octyl Alcohol $\left.\begin{matrix}C_8H_{17}\\H\end{matrix}\right\}O$.—The essential oil of the seeds of cow's parsnip (*Heracleum Spondylium*) contains a large quantity of octyl acetate and some octyl caproate, and the oil of the common parsnip consists chiefly of octyl butyrate. The acetate is a mobile liquid, smelling like oranges and boiling at 207°. On heating these ethers with an alcoholic solution of caustic potash, octyl alcohol is obtained, a colourless liquid, insoluble in water, boiling at 195°, and possessing a strong aromatic smell. On saturating it with hydrochloric acid gas and heating the mixture, *octyl chloride* $C_8H_{17}Cl$ is formed, a liquid boiling at 180°, and possessing a faint odour. *Octyl iodide* $C_8H_{17}I$ boils at 221°; it is obtained by adding iodine gradually to a mixture of the alcohol with amorphous phosphorus, and distilling. By acting on the iodide with zinc and hydrochloric acid, *octane* C_3H_{18} is formed; it is also obtained by the action of sodium upon butyl iodide, and occurs in American petroleum. It boils at 124°.

By treating the alcohol with a solution of potassium dichromate in dilute sulphuric acid, *octylic acid* $C_8H_{16}O_2$ is formed, a crystalline mass, melting at 17° and boiling at 233°. It has a sharp rancid taste and a faint smell, which on heating becomes pungent and sudorific. An acid having the same composition and great resemblance to nonylic acid is *caprylic acid*, which occurs in butter and other fats; it melts at 14°, and boils between 236° and 240°. Ethyl octylate $\left.\begin{matrix}C_8H_{15}O\\C_2H_5\end{matrix}\right\}O$ is formed by adding sulphuric acid to a solution of octylic acid in ethyl alcohol; it boils at 205° and smells like pineapples. *Ethyl caprylate* is a similar liquid, boiling at 214°.

Secondary Octyl Alcohol or Methyl-hexyl Carbinol $\left.\begin{matrix}CH_3\\C_6H_{13}\end{matrix}\right\}CH.OH$, formerly called capryl alcohol, is produced by distilling castor-oil soap with caustic soda. Castor-oil contains ricinoleic acid, which by alkalis is decomposed into the alcohol and sebacic acid:—

$$C_{18}H_{34}O_3 + 2NaOH = C_8H_{18}O + C_{10}H_{16}Na_2O_4 + H_2$$

The distillate contains besides the secondary alcohol other products; it is repeatedly rectified over caustic soda and then subjected to fractional distillation. Methyl-hexyl carbinol is a colourless oily liquid, possessing an aromatic smell, and boiling at 181°. By a dilute solution of chromic acid it is oxidized to methyl-hexyl ketone $\left.\begin{matrix}CH_3\\C_6H_{13}\end{matrix}\right\}CO$, a liquid boiling at 171°. This ketone is sometimes formed as a by-product in the preparation of the alcohol. *Secondary octyl chloride* $C_8H_{17}Cl$ smells like oranges and boils at 173°. The iodide boils at 212°, and yields by the action of nascent hydrogen normal octane.

NONYL GROUP.

This group has been so far very little studied. *Pelargonic acid*, $C_9H_{18}O_2$ occurs in the essential oil of *Pelargonium roseum*, and is also formed by oxidizing *methyl-nonyl ketone*, the chief constituent of oil of rue. This acid has a faint, rancid odour; it melts at 18° and boils at 250°.

Nonylic Acid $\left.\begin{matrix}C_9H_{17}O\\H\end{matrix}\right\}O$.—This acid, which has great resemblance to pelargonic acid, has been prepared by heating octyl iodide with potassium cyanide and decomposing the nitrile thus formed with caustic potash. It fuses at 12° and boils at 254°.

DECATYL GROUP.

Diamyl, or Tetramethyl Hexane $C_6H_{10}(CH_3)_4$ is obtained by decomposing amyl iodide with sodium; it is a colourless mobile liquid, boiling at 158°. On acting on it with chlorine *decatyl chloride* is formed, which, when heated with potassium acetate and acetic acid, yields the acetate, a liquid possessing a pleasant smell like oranges. On decomposing it with an alkali, *decatyl alcohol* $\left.\begin{matrix}C_{10}H_{21}\\H\end{matrix}\right\}O$ is obtained, an oily liquid boiling at about 210°—215°, and smelling like the flowers of *Daphne odorata.* It is most probable that these bodies are mixtures of primary and secondary decatyl compounds.

Capric Acid $\left.\begin{matrix}C_{10}H_{19}O\\H\end{matrix}\right\}O$ occurs in different fats and in fusel-oil. It is a crystalline solid, fusing at 30°, boiling at 270°, and possessing a faint, goat-like smell.

The so-called *œnanthic ether*, which is found in different kinds of wine, and which is *the* cause of the peculiar odour which *all* wines have in common, contains ethyl caprate besides ethyl caprylate, and probably other compound ethers in varying quantities.

HENDECATYL GROUP.

Methyl-nonyl Carbinol $\left.\begin{matrix}CH_3\\C_9H_{19}\end{matrix}\right\}CH.OH$.—This secondary alcohol has been prepared by acting with sodium on an alcoholic solution of methyl-nonyl ketone. It is a thick, colourless liquid, boiling at 229°. By acting on it with bromine and phosphorus the bromide $C_{11}H_{23}Br$ is formed, which on distillation splits up into hydrobromic acid and *hendecatene* $C_{11}H_{22}$, a liquid boiling at 200°.

Methyl-nonyl Ketone $\left.\begin{matrix}CH_3\\C_9H_{10}\end{matrix}\right\}CO$ forms the chief constituent of oil of rue, *Ruta graveolens.* It has been also obtained synthetically by distilling a mixture of calcium acetate and caprate. It is a colourless liquid, boiling at 225° and possessing an aromatic odour.

CETYL GROUP.

Cetyl Alcohol $\left.\begin{matrix}C_{16}H_{33}\\H\end{matrix}\right\}O$.—Spermaceti consists principally of cetyl palmitate; on heating it with an alcoholic potash solution cetyl alcohol is obtained, which forms small white crystals, melting at 50° and volatilizing at a high temperature without decomposition. It is insoluble in water, but readily soluble in alcohol and ether. By heating it with iodine and phosphorus, cetyl iodide is formed, a white crystalline mass, melting at 22° and decomposing at a higher temperature. By acting with sodium on fused cetyl alcohol, *sodium cetylate* $\left.\begin{matrix}C_{16}H_{33}\\Na\end{matrix}\right\}O$ is formed; the latter, when heated with cetyl iodide, yields *dicetyl ether* $\left.\begin{matrix}C_{16}H_{33}\\C_{16}H_{33}\end{matrix}\right\}O$, which crystallizes in shining plates melting at 55°. On passing ammonia into fused cetyl iodide, *tricetylamine*

$(C_{16}H_{33})_3N$ is formed, crystallizing in white needles. Its salts are insoluble in water, but they dissolve in alcohol.

By heating cetyl alcohol with dilute sulphuric acid and potassium dichromate, *palmitaldehyde* $C_{16}H_{32}O$ is formed, a white crystalline solid, melting at 52°, and yielding on further oxidation palmitic acid, which is also formed by heating cetyl alcohol with soda lime:—

$$C_{16}H_{34}O + NaOH = C_{16}H_{31}NaO_2 + 2H_2O$$

This acid, which is found in a great many fats, will be described in the next chapter.

SOLID FATTY ACIDS.

Those fatty acids containing more than ten atoms of carbon are solid bodies, which on distillation undergo partial decomposition. They occur, together with lower members of the series, in different vegetable and animal fats, as compound ethers of the triad radical propenyl C_3H_5. By boiling a fat or oil with caustic potash or soda, *soaps* are formed, which consist of the potassium salts (soft soap), or sodium salts (hard soap) of fatty acids. They are soluble in water, whilst most other salts of the solid fatty acids are insoluble in water.

As all fats contain a mixture of several fatty acids, and as such mixtures are often formed in the oxidation of complex organic compounds as well as by different processes of fermentation, and by putrefaction, it is of importance to be acquainted with the method employed to separate the different constituents from such a mixture.

Fatty acids which volatilize without decomposition are separated by *partial neutralization*. By adding an alkali to such a mixture, the acid containing the least number of carbon atoms, being the stronger, is first neutralized. Thus when to a mixture of butyric acid and valerianic acid a quantity of soda is added which is insufficient to neutralize the acids, and the liquid is subjected to distillation, either pure valerianic acid passes over, or the residue consists of pure sodium butyrate, according to the proportions of the two acids present.

In the former case all the butyric acid, together with some of the valerianic acid, is found in the residue. By adding gradually dilute sulphuric acid, all the valerianic acid is set free before any of the butyrate is decomposed.

In the second case all the valerianic acid and some butyric is contained in the distillate; from which by partial neutralization and redistillation pure valerianic can be obtained. It will be easily understood that by repeating these operations, two or even more volatile fatty acids can be completely separated.

Solid fatty acids may be separated from each other by *fractional precipitation*. The mixture is dissolved in spirits of wine, and an alcoholic solution of lead acetate or magnesium acetate is added in small quantities, by which the acids having the highest molecular weight are first precipitated. To the filtrate again a small quantity of the lead or magnesium salt is added, and this operation repeated until all the acids are precipitated. The different precipitates are decomposed with hydrochloric acid, and if necessary again treated in the same way until pure acids are obtained. The purity of an acid thus separated is easily recognized by subjecting it again to fractional precipitation ; when pure, the first precipitate yields an acid having the same composition and melting-point as that obtained from the last precipitate.

Pure acids melt and solidify at the same temperature, whilst the melting-point of a mixture is not only always lower than that of the most fusible constituent, but the temperature at which it again solidifies is always lower than that at which it melts. Thus the melting-point of stearic acid is 69·2°, and that of palmitic acid 62°, whilst a mixture consisting of 30 parts of stearic acid and 70 parts of palmitic acid melts at 55°·1, and solidifies again at 54°.

Lauric Acid $C_{12}H_{24}O$ occurs in the fat contained in the berries of the bay-tree (*Laurus nobilis*), in pichurim beans, and also in cocoa-nut oil. It forms white needles melting at 43°·6.

Myristic Acid $C_{14}H_{28}O_2$ is found in nutmeg butter, in spermaceti, and other fats. It crystallizes in white needles melting at 53°·8.

Palmitic Acid $C_{16}H_{32}O_2$ is one of the chief constituents of the different kinds of tallow, of spermaceti, palm oil, olive oil, and a great number of other fats. It is best obtained from palm-oil soap, a mixture of sodium palmitate and stearate, by dissolving it in alcohol and separating the acids by fractional precipitation.

Palmitic acid crystallizes in shining scales and melts at 62°.

Margaric Acid $C_{17}H_{34}O_2$.—This name was originally given to an acid supposed to exist in several fats, but it has since been shown that the so-called margaric acid is only a mixture of palmitic and stearic acids. Margaric acid does not appear to exist in natural fats, but has been produced artificially by heating cetyl iodide with potassium cyanide, and decomposing the *margaronitrile* thus formed with alcoholic potash. It has great resemblance to palmitic acid.

Stearic Acid $C_{18}H_{36}O_2$ occurs, together with palmitic acid and other acids, in suet, tallow, cocoa-nut oil, cocoa butter, in human fat, in the fat of the goose, &c. &c. It is easily obtained from tallow-soap by dissolving it in six parts of hot water, and adding to the solution 40—50 parts of cold water. A mixture of acid sodium stearate and palmitate separates in shining scales. On crystallizing this mixture from hot alcohol the stearate separates first, and may be purified by recrystallization. On decomposing this salt by hydrochloric acid, and recrystallizing the acid from hot alcohol it is obtained in nacreous needles or laminæ, melting at 69°·2, and solidifying to a crystalline scaly mass.

The stearin-candles consist of a mixture of stearic and palmitic acids.

Arachidic Acid $C_{20}H_{40}O_2$ occurs in the fat of the earth-nut (*Arachis hypogæa*), and *behenic acid* $C_{22}H_{44}O_4$ in the oil from the fruits of *Moringa nux Behen*. *Hyænic acid* $C_{25}H_{50}O_2$ was found in the fat from the glands of a diseased striated hyæna.

CHINESE WAX AND BEES'-WAX.

Chinese wax, the product of an insect (*Coccus ceriferus*), is a white crystalline substance resembling spermaceti, and consisting almost entirely of *ceryl cerotate* $\left.\begin{matrix} C_{27}H_{55} \\ C_{27}H_{53}O \end{matrix}\right\} O$. By saponifying it with solid caustic potash, dissolving the soap in hot water, and adding barium chloride, a mixture of ceryl alcohol and barium cerotate is precipitated, which may be separated by exhausting the dry precipitate with hot alcohol, in which the barium salt is insoluble. *Ceryl alcohol* $\left.\begin{matrix} C_{27}H_{55} \\ H \end{matrix}\right\} O$ is a white crystalline substance, melting at 79°, and distilling at a high temperature with partial decomposition into water and *cerotene* $C_{27}H_{54}$. When ceryl alcohol is heated with caustic potash, it is oxidized to cerotic acid :—

$$\left.\begin{matrix} C_{27}H_{55} \\ H \end{matrix}\right\} O + KOH = \left.\begin{matrix} C_{27}H_{53}O \\ K \end{matrix}\right\} O + H_2$$

Cerotic Acid $C_{27}H_{54}O$ is also found in the free state in bees'-wax, and may be extracted from it with boiling alcohol. It forms crystalline grains melting at 78°.

The portion of bees'-wax insoluble in alcohol consists of *myricyl palmitate* $\left.\begin{matrix} C_{30}H_{61} \\ C_{16}H_{31}O \end{matrix}\right\} O$. On heating it with alcoholic potash, and dissolving the residue left on the evaporation of the alcohol in hot water, and adding dilute hydrochloric acid, a mixture of myricyl alcohol and palmitic acid is precipitated. To separate them they are dissolved in hot alcohol; on cooling *myricyl alcohol* $\left.\begin{matrix} C_{30}H_{61} \\ H \end{matrix}\right\} O$ separates in silky crystals, melting at 80°. By heating this alcohol with soda-lime it is oxidized to *melissic acid* $C_{30}H_{60}O$, a body bearing great resemblance to cerotic acid, but melting at 80°. Melissic acid has not been found in nature.

COMPOUNDS OF DYAD RADICALS.

DYAD ALCOHOL-RADICALS.

By depriving the paraffins of two atoms of hydrogen a series of hydrocarbons is obtained having the general formula C_nH_{2n}, to which the name the *Olefines* has been given (from olefiant gas, an old name of ethene, the first hydrocarbon of the series). The names of the olefines are derived from those of the paraffins by changing the final *-ane* into *-ene* :—

Ethane . .	C_2H_6	Ethene . .	C_2H_4
Propane . .	C_3H_8	Propene . .	C_3H_6

A general method of obtaining olefines consists in the abstraction of the elements of water from the monad alcohols. This may be effected by means of sulphuric acid, zinc chloride, and other dehydrating agents :—

$$C_2H_6O - H_2O = C_2H_4$$
$$C_5H_{12}O - H_2O = C_5H_{10}$$

Olefines are also produced by heating the haloid compounds of monad alcohol radicals with a solution of caustic potash in spirits of wine :—

$$C_6H_{13}Cl + KOH = C_6H_{12} + H_2O + KCl$$

Of other reactions by which olefines are formed the following may be mentioned.

By acting on the iodides of the monad alcohol radicals with nascent hydrogen, or with sodium or zinc, not only are paraffins formed, but also olefines in smaller quantities. Thus when ethyl iodide is heated with zinc, not only is butane formed but also *ethane* and *ethene* :—

$$2C_2H_5I + Zn = C_2H_6 + C_2H_4 + ZnI_2$$

By the action of zinc and hydrochloric acid upon secondary hexyl iodide, *hexane* C_6H_{14} is formed as the chief product, but at the same time some *hexene* C_6H_{12} and some *dihexyl* $C_{12}H_{26}$ are produced :—

$$(1) \quad C_6H_{13}I + H_2 = C_6H_{14} + IH$$
$$(2) \quad 2C_6H_{13}I + Zn = C_6H_{14} + C_6H_{12} + ZnI_2$$
$$(3) \quad 2C_6H_{13}I + Zn = C_{12}H_{26} + ZnI_2$$

---

[1] Formerly they were designated by names derived from those of the monad alcohol radicals by the addition of -ene : thus ethene is still frequently called ethylene, &c.

Olefines may also be produced by synthesis. Thus *pentene* C_5H_{10} has been obtained by the action of zinc-ethyl upon allyl iodide C_3H_5I :—

$$(C_2H_5)_2Zn + 2C_3H_5I = 2C_5H_{10} + ZnI_2$$

By heating monobromethene with zinc-ethyl, *butene* C_4H_8 is produced:—

$$2(C_2H_3Br) + (C_2H_5)_2Zn = 2C_4H_8 + ZnBr_2$$

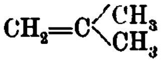
Olefines also occur amongst the products of destructive distillation of many organic bodies, and are found therefore in coal-tar, wood-tar, &c.

In their physical properties the olefines have great resemblance to the paraffins. The lowest members of the series are gaseous at the ordinary temperature; most of the others are liquids having a faint ethereal and garlic-like smell; and the highest members consist of crystalline solids.

The olefines contain two carbon atoms linked together by two combining units of each atom. The number of isomerides which according to theory may exist is larger than that of the paraffins, as the double linking of two carbon atoms can take place between different atoms in the carbon chain. Thus we know only two hydrocarbons C_4H_{10}, but three having the formula C_4H_8 :—

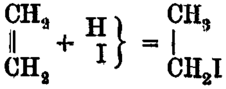
$$CH_2{=}CH{-}CH_2{-}CH_3$$

$$CH_3{-}CH{=}CH{-}CH_3$$



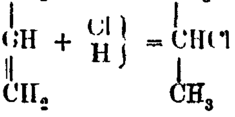
$$CH_2{=}C\begin{cases}CH_3\\CH_3\end{cases}$$

The most characteristic property of the olefines is that they combine directly with one molecule of another element or compound, as with the hydracids of the chlorine group, ethene and hydriodic acid yielding ethyl iodide :—

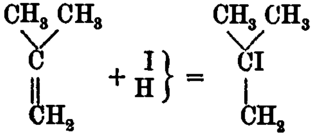


$$\begin{array}{c}CH_2\\ \| \\ CH_2\end{array} + \left.\begin{array}{c}H\\I\end{array}\right\} = \begin{array}{c}CH_3\\ | \\ CH_2I\end{array}$$

The olefines containing more than two atoms of carbon yield by this reaction secondary or tertiary compounds :—

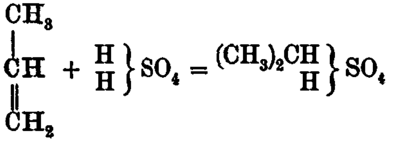


$$\begin{array}{c}CH_3\\ | \\ CH\\ \| \\ CH_2\end{array} + \left.\begin{array}{c}Cl\\H\end{array}\right\} = \begin{array}{c}CH_3\\ | \\ CHCl\\ | \\ CH_3\end{array}$$



Olefines combine also with concentrated sulphuric acid :—

$$C_2H_4 + \left.\begin{matrix}H\\H\end{matrix}\right\}SO_4 = \left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}SO_4$$



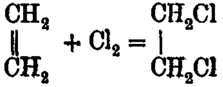
$$\begin{array}{l}CH_3\\ \mid\\ CH\\ \parallel\\ CH_2\end{array} + \left.\begin{matrix}H\\H\end{matrix}\right\}SO_4 = \left.\begin{matrix}(CH_3)_2CH\\H\end{matrix}\right\}SO_4$$

The haloïd ethers of the dyad radicals are very readily produced by the direct union of the olefines with the elements of the chlorine group :—

$$C_2H_4 + Cl_2 = C_2H_4Cl_2$$
$$C_3H_6 + Br_2 = C_3H_6Br_2$$

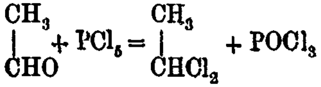
Besides these addition-products there exist also isomeric compounds, formed by substitution of hydrogen or oxygen in saturated compounds. Thus by acting with chlorine on ethane we obtain as the second product of substitution *dichlorethane* or *ethidene dichloride*, which is an isomeride of ethene dichloride, and has also been produced by the action of phosphorus pentachloride on aldehyde. The constitution of these two isomerides is explained by their mode of formation :—

Ethene Dichloride.



$$\begin{array}{l}CH_2\\ \parallel\\ CH_2\end{array} + Cl_2 = \begin{array}{l}CH_2Cl\\ \mid\\ CH_2Cl\end{array}$$

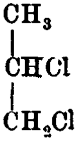
Ethidene Dichloride.



$$\begin{array}{l}CH_3\\ \mid\\ CHO\end{array} + PCl_5 = \begin{array}{l}CH_3\\ \mid\\ CHCl_2\end{array} + POCl_3$$

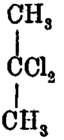
Propidene dichloride, an isomeride of propene dichloride, is produced by treating acetone with phosphorus pentachloride :—

Propene Dichloride.



$$\begin{array}{l}CH_3\\ \mid\\ CHCl\\ \mid\\ CH_2Cl\end{array}$$

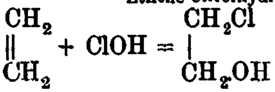
Propidene Dichloride.



$$\begin{array}{l}CH_3\\ \mid\\ CCl_2\\ \mid\\ CH_3\end{array}$$

The olefines also combine with hypochlorous and hypobromous acids, forming compounds which at the same time are haloïd ethers and alcohols:—

Ethene Chlorhydrate.



$$\begin{array}{l}CH_2\\ \|\\ CH_2\end{array} + ClOH = \begin{array}{l}CH_2Cl\\ |\\ CH_2OH\end{array}$$

The alcohols of the dyad radicals, called *glycols* (on account of their sweet taste), are produced by reactions quite analogous to those by which the monad alcohols are obtained from their haloïd ethers. Thus ethene iodide yields with silver acetate, ethene diacetate:—

$$C_2H_4\left\{\begin{array}{l}I\\ I\end{array}\right. + 2AgO.C_2H_3O = C_2H_4\left\{\begin{array}{l}OC_2H_3O\\ OC_2H_3O\end{array}\right. + 2AgI$$

Alkalis decompose this acetate, ethene alcohol or common glycol being formed:—

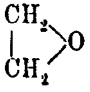
$$C_2H_4\left\{\begin{array}{l}OC_2H_3O\\ OC_2H_3O\end{array}\right. + Ba\left\{\begin{array}{l}OH\\ OH\end{array}\right. = C_2H_4\left\{\begin{array}{l}OH\\ OH\end{array}\right. + Ba\left\{\begin{array}{l}OC_2H_3O\\ OC_2H_3O\end{array}\right.$$

The reaction of the glycols are for the most part similar to those of the alcohols of monad radicals, but inasmuch as the former contain two hydroxyls, the reactions generally take place in two stages, and yield two series of compounds:—

Ethene Chlorhydrate. $C_2H_4\left\{\begin{array}{l}Cl\\ OH\end{array}\right.$	Ethene Dichloride. $C_2H_4\left\{\begin{array}{l}Cl\\ Cl\end{array}\right.$
Ethene Monacetate. $C_2H_4\left\{\begin{array}{l}OH\\ OC_2H_3O\end{array}\right.$	Ethene Diacetate. $C_2H_4\left\{\begin{array}{l}OC_2H_3O\\ OC_2H_3O\end{array}\right.$
Sodium Ethenate. $C_2H_4\left\{\begin{array}{l}OH\\ ONa\end{array}\right.$	Disodium Ethenate. $C_2H_4\left\{\begin{array}{l}ONa\\ ONa\end{array}\right.$
Ethyl Ethenate. $C_2H_4\left\{\begin{array}{l}OH\\ OC_2H_5\end{array}\right.$	Diethyl Ethenate. $C_2H_4\left\{\begin{array}{l}OC_2H_5\\ OC_2H_5\end{array}\right.$
Ethene Oxyhydrosulphide. $C_2H_4\left\{\begin{array}{l}OH\\ SH\end{array}\right.$	Ethene Dihydrosulphide. $C_2H_4\left\{\begin{array}{l}SH\\ SH\end{array}\right.$

The two hydroxyls may also be replaced by one atom of a dyad element or a dyad radical; whilst the olefines can, like the monad radicals, substitute hydrogen in ammonia, &c.:—

Ethene Oxide.



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

Ethenediamine.

$$C_2H_4\left\{\begin{array}{l}NH_2\\ NH_2\end{array}\right.$$

Triethenediamine

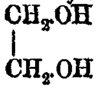
$$\left.\begin{array}{l}C_2H_4\\ C_2H_4\\ C_2H_4\end{array}\right\}\begin{array}{l}N\\ \\ N\end{array}$$

The following table contains the olefines and glycols which have been best examined :—

Olefines.			Glycols.		
		Boiling-point.			Boiling-point.
Ethene	C_2H_4	—	Ethene Glycol	$C_2H_6O_2$	197°·5
Propene	C_3H_6	—	Propene „	$C_3H_8O_2$	188
Isobutene	C_4H_8	− 7°	Isobutene „	$C_4H_{10}O_2$	183
Butene		+ 3			
Amylene	C_5H_{10}	35	Amylene „	$C_5H_{12}O_2$	177
Pentene		40			
Hexene	C_6H_{12}	70	Hexene „	$C_6H_{14}O_2$	207
Heptene	C_7H_{14}	100			
Octene	C_8H_{16}	125	Octene „	$C_8H_{18}O_2$	237
Diamylene	$C_{10}H_{20}$	158			
Hendecadene	$C_{11}H_{22}$	200			
Cetene	$C_{16}H_{32}$	275			
Cerotene	$C_{27}H_{54}$	—			
Melene	$C_{30}H_{60}$	—			

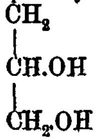
The boiling-points of the first four glycols become lower as the molecular weight increases. This apparent anomaly is easily explained by the different constitution of these bodies; ethene glycol being a primary alcohol, while the others are primary as well as secondary or tertiary compounds :—

Ethene Glycol.



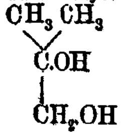
$$\begin{array}{l} CH_2.OH \\ | \\ CH_2.OH \end{array}$$

Propene Glycol.



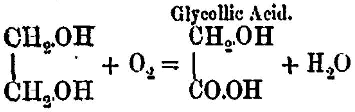
$$\begin{array}{l} CH_3 \\ | \\ CH.OH \\ | \\ CH_2.OH \end{array}$$

Isobutene Glycol.

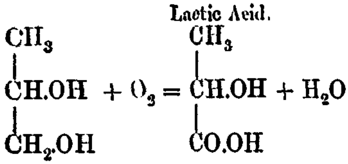


MONOBASIC ACIDS OF THE SERIES $C_nH_{2n}O_3$.

These acids are derived from the glycols by replacing in the latter two atoms of hydrogen by one of oxygen, and may be produced by the slow oxidation of glycols :—

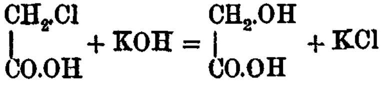


$$\begin{array}{l} CH_2.OH \\ | \\ CH_2.OH \end{array} + O_2 = \overset{\text{Glycollic Acid.}}{\begin{array}{l} CH_2.OH \\ | \\ CO.OH \end{array}} + H_2O$$

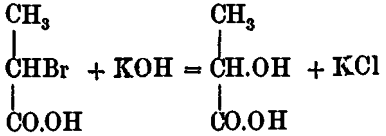


$$\begin{array}{l} CH_3 \\ | \\ CH.OH \\ | \\ CH_2.OH \end{array} + O_2 = \overset{\text{Lactic Acid.}}{\begin{array}{l} CH_3 \\ | \\ CH.OH \\ | \\ CO.OH \end{array}} + H_2O$$

They are also formed by replacing in a fatty acid one atom of hydrogen by one of hydroxyl. This can be easily effected by the action of alkalis or silver oxide and water on the monobrominated or chlorinated fatty acids; thus monochloracetic acid yields glycollic or oxacetic acid, and monobromopropionic acid is converted into lactic or oxypropionic acid:—



$$\begin{array}{l} CH_2.Cl \\ | \\ CO.OH \end{array} + KOH = \begin{array}{l} CH_2.OH \\ | \\ CO.OH \end{array} + KCl$$



$$\begin{array}{l} CH_3 \\ | \\ CHBr \\ | \\ CO.OH \end{array} + KOH = \begin{array}{l} CH_3 \\ | \\ CH.OH \\ | \\ CO.OH \end{array} + KCl$$

On the other hand, by treating glycollic or lactic acid with hydrochloric or hydrobromic acids they are again converted into the corresponding substituted fatty acids. Hydriodic acid acts in a similar way, but the moniodo-acids thus formed are readily further acted upon by the hydriodic acid, and reduced to a fatty acid. Lactic acid can thus be easily converted into propionic acid:—

$$(1)\quad C_3H_5(OH)O_2 + HI = C_3H_5IO_2 + H_2O$$

$$(2)\quad C_3H_5IO_2 \quad + HI = C_3H_6O_2 \ + I_2$$

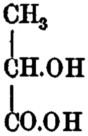
The acids of the glycollic series being at the same time monobasic acids and monad alcohols, form different kinds of haloïd and other ethers, of amides, &c.

Thus *monochloropropionic acid* must be regarded as an alcoholic chloride; by acting on it with ammonia, we obtain *amidopropionic acid* or *alanine*, which being an amine combines with acids, but at the same time, as a monobasic acid, it forms also metallic salts.

By heating lactic acid with absolute alcohol we get ethyl lactate, a neutral volatile liquid, which is readily acted upon by sodium like other alcohols, the hydrogen of the hydroxyl being replaced by the metal. Ethyl iodide converts this sodium-compound into *diethyl lactate*, which by alkalis is resolved into ethyl alcohol and a salt of *ethyl-lactic acid*, an isomeride of ethyl lactate, from which it, however, differs by being as powerful an acid as lactic acid itself. Ammonia converts diethyl lactate into *lactamide*, a neutral body, which is isomeric with *alanine*. When a metallic lactate is treated with phosphorus pentachloride, it yields *lactyl chloride*, a body having the character of an alcoholic chloride as well as that of an acid chloride, and being therefore resolved by water into hydrochloric acid and monochloropropionic acid.

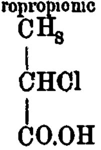
The following formulæ explain the constitution of these different compounds:—

Lactic Acid.



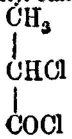
$$\begin{array}{l} CH_3 \\ | \\ CH.OH \\ | \\ CO.OH \end{array}$$

Chloropropionic Acid.



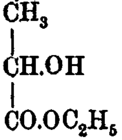
$$\begin{array}{l} CH_3 \\ | \\ CHCl \\ | \\ CO.OH \end{array}$$

Lactyl Chloride.



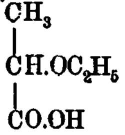
$$\begin{array}{l} CH_3 \\ | \\ CHCl \\ | \\ COCl \end{array}$$

Ethyl Lactate.



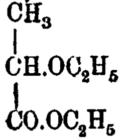
$$\begin{array}{l} CH_3 \\ | \\ CH.OH \\ | \\ CO.OC_2H_5 \end{array}$$

Ethyllactic Acid.



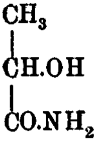
$$\begin{array}{l} CH_3 \\ | \\ CH.OC_2H_5 \\ | \\ CO.OH \end{array}$$

Diethyl Lactate.



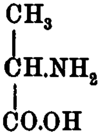
$$\begin{array}{l} CH_3 \\ | \\ CH.OC_2H_5 \\ | \\ CO.OC_2H_5 \end{array}$$

Lactamide.



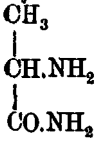
$$\begin{array}{l} CH_3 \\ | \\ CH.OH \\ | \\ CO.NH_2 \end{array}$$

Alanine.



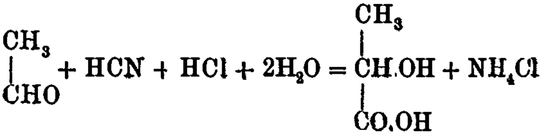
$$\begin{array}{l} CH_3 \\ | \\ CH.NH_2 \\ | \\ CO.OH \end{array}$$

Lactyldiamide.



$$\begin{array}{l} CH_3 \\ | \\ CH.NH_2 \\ | \\ CO.NH_2 \end{array}$$

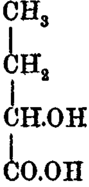
The acids of this group can be obtained synthetically by heating an aldehyde with hydrocyanic acid and dilute hydrochloric acid; acetaldehyde yielding lactic acid:—



$$\begin{array}{l} CH_3 \\ | \\ CHO \end{array} + HCN + HCl + 2H_2O = \begin{array}{l} CH_3 \\ | \\ CH.OH \\ | \\ CO.OH \end{array} + NH_4Cl$$

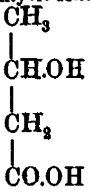
Many acids of this series are known in several isomeric modifications; the cause of the isomerism being either a different grouping of the carbon atoms, or the alcoholic hydroxyl occupying another position. Thus we know three oxybutyric acids:—

α Oxybutyric Acid.



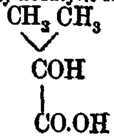
$$\begin{array}{l} CH_3 \\ | \\ CH_2 \\ | \\ CH.OH \\ | \\ CO.OH \end{array}$$

β Oxybutyric Acid.

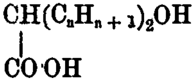


$$\begin{array}{l} CH_3 \\ | \\ CH.OH \\ | \\ CH_2 \\ | \\ CO.OH \end{array}$$

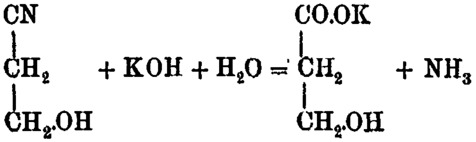
Oxy-isobutyric Acid.



Oxy-isobutyric acid is not only obtained by the action of moist silver oxide on monobromisobutyric acid, but has also been produced by replacing in *oxalic acid* $\begin{array}{l} CO{\cdot}OH \\ | \\ CO{\cdot}OH \end{array}$ one atom of oxygen by two of methyl. This is done by heating methyl oxalate with zinc-methyl.

By employing the zinc-compounds of other alcohol-radicals, a great number of such *isolactic acids*  $\begin{matrix}CH(C_nH_{n+1})_2OH\\ |\\ CO{\cdot}OH\end{matrix}$ have been prepared.

The acids of the lactic series which have so far been described are secondary alcohols with the exception of glycollic acid, which is a primary alcohol. An acid having a similar constitution is *ethene-lactic acid,* which has been produced by heating ethene chlorhydrate with potassium cyanide, and decomposing the nitrile thus formed with caustic potash:—



$$\begin{matrix}CN\\ |\\ CH_2\\ |\\ CH_2.OH\end{matrix} + KOH + H_2O = \begin{matrix}CO.OK\\ |\\ CH_2\\ |\\ CH_2.OH\end{matrix} + NH_3$$

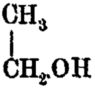
Ethene-lactic acid corresponds to primary propyl alcohol and yields by oxidation bibasic malonic acid, whilst common or *ethidene-lactic acid,* which corresponds to secondary propyl alcohol, is resolved by oxidizing agents into acetic acid and carbon dioxide.

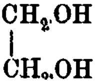
Glycollic acid and the two lactic acids occur in nature.

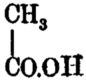
BIBASIC ACIDS OF THE SERIES $C_nH_{2n-2}O_4$.

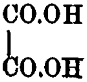
Oxalic Acid	$C_2H_2O_4$	Suberic Acid . .	$C_8H_{14}O_4$
Malonic "	$C_3H_4O_4$	Azelaic " . .	$C_9H_{16}O_4$
Succinic "	$C_4H_6O_4$	Sebacic " . .	$C_{10}H_{18}O_4$
Desoxyglutanic "	$C_5H_8O_4$	Brassic " . .	$C_{11}H_{20}O_4$
Adipic "	$C_6H_{10}O_4$	Rocellic " . .	$C_{17}H_{32}O_4$
Pimelic "	$C_7H_{12}O_4$		

The acids of this group are bibasic, containing the group carboxyl twice; they stand in the same relation to primary glycols as the fatty acids to the monad primary alcohols:—

Ethyl Alcohol 
$\begin{matrix}CH_3\\ |\\ CH_2.OH\end{matrix}$

Ethene Alcohol 
$\begin{matrix}CH_2.OH\\ |\\ CH_2.OH\end{matrix}$

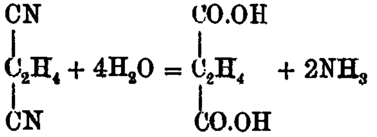
Acetic Acid 
$\begin{matrix}CH_3\\ |\\ CO.OH\end{matrix}$

Oxalic Acid 
$\begin{matrix}CO.OH\\ |\\ CO.OH\end{matrix}$

It has already been mentioned that with the exception of ethene glycol other primary glycols are hardly known. On oxidizing ethene glycol it first yields monobasic glycollic acid, which by further oxidation is converted into oxalic acid. The second acid of the series, malonic acid, is formed by oxidizing ethene-lactic acid, which has to be regarded as the first oxidation-product of primary propene glycol.

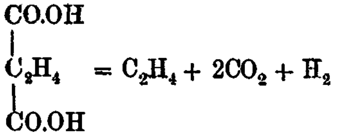
All acids of this series with the exception of oxalic acid contain an olefine combined with two carboxyls. This is shown not only by the different modes of formation of these acids, but also by many of their decompositions.

When ethene bibromide is heated with potassium cyanide the nitrile of succinic acid is formed, and this compound, by the action of caustic potash, yields the latter acid :—



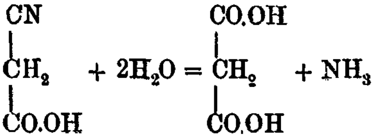
$$\begin{array}{l}\mathrm{CN}\\ |\\ \mathrm{C_2H_4}\\ |\\ \mathrm{CN}\end{array} + 4\mathrm{H_2O} = \begin{array}{l}\mathrm{CO.OH}\\ |\\ \mathrm{C_2H_4}\\ |\\ \mathrm{CO.OH}\end{array} + 2\mathrm{NH_3}$$

When a galvanic current is passed through a solution of potassium succinate, the acid is decomposed into ethene, carbon dioxide and hydrogen :—



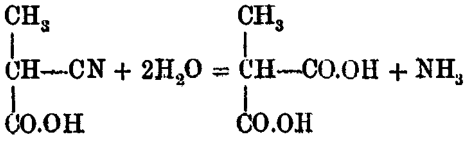
$$\begin{array}{l}\mathrm{CO.OH}\\ |\\ \mathrm{C_2H_4}\\ |\\ \mathrm{CO.OH}\end{array} = \mathrm{C_2H_4} + 2\mathrm{CO_2} + \mathrm{H_2}$$

The chlorine in chloracetic acid may be replaced by cyanogen, and thus *cyanacetic acid* is formed, a compound being a monobasic acid as well as a nitrile, and yielding *malonic acid* by the action of alkalis :—



$$\begin{array}{l}\mathrm{CN}\\ |\\ \mathrm{CH_2}\\ |\\ \mathrm{CO.OH}\end{array} + 2\mathrm{H_2O} = \begin{array}{l}\mathrm{CO.OH}\\ |\\ \mathrm{CH_2}\\ |\\ \mathrm{CO.OH}\end{array} + \mathrm{NH_3}$$

a Cyanopropionic acid is converted by the same reaction into *isosuccinic acid* :—

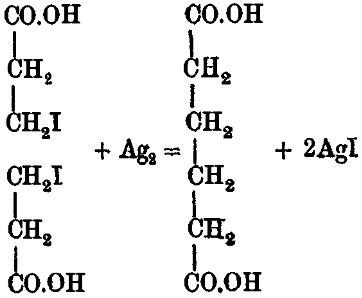


$$\begin{array}{l}\mathrm{CH_3}\\ |\\ \mathrm{CH{-}CN}\\ |\\ \mathrm{CO.OH}\end{array} + 2\mathrm{H_2O} = \begin{array}{l}\mathrm{CH_3}\\ |\\ \mathrm{CH{-}CO.OH}\\ |\\ \mathrm{CO.OH}\end{array} + \mathrm{NH_3}$$

By heating, *a iodopropionic acid* with finely divided silver[1] *adipic acid* is formed :—

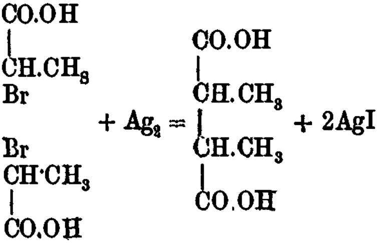
---

[1] The finely divided silver, or *silver-dust*, which is employed for many similar synthetical reactions, is prepared by precipitating a cold dilute solution with hydrochloric acid, and reducing the silver chloride with zinc. The product is washed with dilute hydrochloric acid and water, and dried at a gentle heat. It forms a very fine dark powder, without metallic lustre.



$$\begin{array}{l} \mathrm{CO.OH} \\ | \\ \mathrm{CH_2} \\ | \\ \mathrm{CH_2I} \\ \\ \mathrm{CH_2I} \\ | \\ \mathrm{CH_2} \\ | \\ \mathrm{CO.OH} \end{array} + Ag_2 = \begin{array}{l} \mathrm{CO.OH} \\ | \\ \mathrm{CH_2} \\ | \\ \mathrm{CH_2} \\ | \\ \mathrm{CH_2} \\ | \\ \mathrm{CH_2} \\ | \\ \mathrm{CO.OH} \end{array} + 2AgI$$

By the same reaction, *β bromopropionic acid* is converted into *dimethyl-succinic acid* :—



$$\begin{array}{l} \mathrm{CO.OH} \\ | \\ \mathrm{CH.CH_3} \\ \mathrm{Br} \\ \\ \mathrm{Br} \\ \mathrm{CH{\cdot}CH_3} \\ | \\ \mathrm{CO.OH} \end{array} + Ag_2 = \begin{array}{l} \mathrm{CO.OH} \\ | \\ \mathrm{CH.CH_3} \\ | \\ \mathrm{CH.CH_3} \\ | \\ \mathrm{CO.OH} \end{array} + 2AgI$$

Many of the acids belonging to this group are formed by the oxidation of fats and other bodies. Three of them occur in nature, viz. oxalic acid, succinic acid, and rocellic acid.

ETHENE COMPOUNDS.

ETHENE C_2H_4.

This hydrocarbon is formed, together with many other products, by the destructive distillation of organic bodies, as fats, resins, wood, coal, &c. To obtain pure ethene a mixture of one volume of strong alcohol and 3—4 volumes of concentrated sulphuric acid is gently heated, and the gas washed with concentrated sulphuric acid and a solution of caustic soda, in order to free it from the vapours of alcohol and ether, and from carbon dioxide and sulphur dioxide, which two gases are always formed towards the end of the reaction.

Ethene is a colourless gas having a peculiar faint and suffocating odour. It condenses at − 110° to a liquid; it is very inflammable, burning with a bright luminous flame.

It was formerly called *olefiant gas*, because it combines with chlorine to form ethene dichloride, an oily liquid. Ethene also combines readily with bromine, but more difficultly with iodine. The concentrated hydracids of these elements also combine with ethene, forming haloïd ethers of ethyl. By shaking it with concentrated sulphuric acid it is dissolved, ethylsulphuric acid being formed. Aqueous hypochlorous and hypobromous acids also absorb the gas slowly.

When ethene is passed into a solution of platinum dichloride and hydrochloric acid, the compound $C_2H_4PtCl_2$ is formed, remaining on evaporation as a brown gum-like mass. *Ethene-platinum chloride* combines with bases and the chlorides of the alkali-metals, forming crystallized compounds. *Potassium-ethene-platinum chloride* $C_2H_4PtCl_2.KCl + H_2O$ crystallizes in large lemon-yellow plates.

Ethene Dichloride $C_2H_4Cl_2$.—Ethene was discovered in the year 1795 by four Dutch chemists, who found that this gas readily combines with chlorine, forming an oily liquid, which still is known by the name of *Dutch liquid*.

To prepare ethene dichloride, equal volumes of ethene and chlorine are passed into a large glass globe, provided at the lower end with an open tubulus, through which the dichloride runs into a flask. It may also be prepared by passing ethene into a mixture of manganese dioxide, salt, and dilute sulphuric acid as long as the gas is absorbed, and then distilling the dichloride off.

Ethene dichloride is also formed in quantity, together with ethyl chloride and dichlorethane, as a by-product in the manufacture of chloral.

Ethene dichloride is a mobile, colourless liquid smelling like chloroform, and boiling at 85°; at 0° it has the specific gravity 1·271. When it is heated with an alcoholic solution of potash it loses one molecule of hydrochloric acid, and *monochlorethene* or *vinyl chloride* C_2H_3Cl escapes as a gas, which at $-18°$ condenses to a liquid. This compound combines like ethene again with one molecule of chlorine, forming *monochlorethene dichloride* $C_2H_3Cl.Cl_2$, which is acted upon by alcoholic potash with the formation of *dichlorethene* $C_2H_2Cl_2$. By repeating this reaction the following substitution-products have been obtained:—

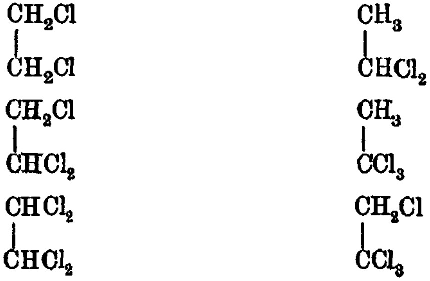
		Boiling-point.
Monochlorethene	C_2H_3Cl	$-18°$
Dichlorethene	$C_2H_2Cl_2$	$+37$
Trichlorethene	$C_2H\,Cl_3$	88
Tetrachlorethene	C_2Cl_4	117

On combining these chlorethenes with chlorine a series of compounds are formed having the same composition as the chlorine substitution-products of ethene:—

From Ethene.	Boiling-point.	From Ethane.	Boiling-point.
$C_2H_4Cl_2$ . . .	85°	$C_2H_4Cl_2$ . . .	59°
$C_2H_3Cl_3$ . . .	115	$C_2H_3Cl_3$ . . .	75
$C_2H_2Cl_4$ . . .	147	$C_2H_2Cl_4$ . . .	127
$C_2H\,Cl_5$ . . .	158	$C_2H\,Cl_5$ . . .	158
C_2Cl_6 . . .	182	C_2Cl_6 . . .	182

From this table it is seen that the three first derivatives of ethane are isomeric with those of ethene, the constitution of these bodies being—

From Ethene. From Ethane.



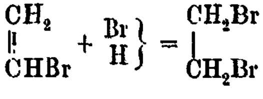
$$\begin{array}{lcl} CH_2Cl & & CH_3 \\ | & & | \\ CH_2Cl & & CHCl_2 \\ CH_2Cl & & CH_3 \\ | & & | \\ CHCl_2 & & CCl_3 \\ CHCl_2 & & CH_2Cl \\ | & & | \\ CHCl_2 & & CCl_3 \end{array}$$

But the compounds 4 and 5 are identical in both series, only one formula being possible for each of them :—

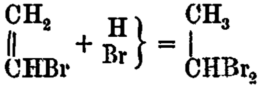
$$\begin{array}{lcl} CHCl_2 & & CCl_3 \\ | & & | \\ CCl_3 & & CCl_3 \end{array}$$

Ethene Dibromide $C_2H_4Br_2$.—This compound forms the starting-point for the preparation of most other ethene compounds. It is most conveniently prepared by the following process. A Winchester quart bottle is filled with ethene; 120 grams of bromine and the same quantity of water are added, and the bottle is quickly closed with a cork through which a glass tube passes, open at both ends, one of which reaches to the bottom of the bottle whilst the other is connected with a gasholder filled with ethene. On shaking the bottle the ethene is absorbed, and as soon as all the bromine has combined, more of it is added, and this process continued until a sufficient quantity of the dibromide has been formed. The product is washed with caustic soda, and dried by distilling it with sulphuric acid.

Ethene dibromide is a colourless liquid, having a sweetish smell and taste, boiling at 129°, and solidifying at 0° to a crystalline mass. When heated with alcoholic potash it yields *monobromethene* C_2H_3Br, a volatile liquid boiling at 24°, and combining with highly concentrated hydrobromic acid to form ethene dibromide, whilst with a more dilute acid it forms the isomeric ethidene bromide :—

(1)


$$\begin{array}{l} CH_2 \\ \| \\ CHBr \end{array} + \left.\begin{array}{l} Br \\ H \end{array}\right\} = \begin{array}{l} CH_2Br \\ | \\ CH_2Br \end{array}$$

(2)


$$\begin{array}{l} CH_2 \\ \| \\ CHBr \end{array} + \left.\begin{array}{l} H \\ Br \end{array}\right\} = \begin{array}{l} CH_3 \\ | \\ CHBr_2 \end{array}$$

Ethene Di-iodide $C_2H_4I_2$.—Ethene combines with iodine slowly at a gentle heat, or when exposed to the light of the sun. This compound can, however, be obtained in quantity by passing ethene into a mixture of absolute alcohol and iodine until the latter is dissolved. More iodine is now added, and the gas passed again into the liquid, and the same process repeated until a magma of crystals has been produced. After the mother liquor has been drained off the crystals are washed with alcohol.

Ethene di-iodide forms white needles, melting at 73°, and subliming with partial decomposition at 80°. When exposed to the light it soon assumes a brown colour. It possesses an ethereal odour, and its vapour attacks the eyes and produces headache.

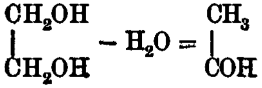
When ethene is passed into iodine monochloride, *ethene chloriodide* C_2H_4ClI is formed, a liquid boiling at 146°.

Ethene Alcohol or Ethene Glycol $C_2H_4(OH)_2$.—To prepare this compound, silver acetate is added to a mixture of ethene di-iodide and glacial acetic acid; a violent reaction sets in and *ethene diacetate* is formed, $C_2H_4\left\{\begin{matrix}OC_2H_3O\\ OC_2H_3O\end{matrix}\right.$, a colourless liquid boiling at 187°. By treating this ether with alkalis, ethene alcohol is produced. This compound is more conveniently obtained by heating an alcoholic solution of ethene dibromide with potassium acetate in closed vessels in a water-bath:—

$$C_2H_4\left\{\begin{matrix}Br\\ Br\end{matrix}\right. + \left.\begin{matrix}C_2H_5\\ H\end{matrix}\right\}O + 2KOC_2H_3O$$
$$= C_2H_4\left\{\begin{matrix}OH\\ O.C_2H_3O\end{matrix}\right. + \left.\begin{matrix}C_2H_5\\ C_2H_3O\end{matrix}\right\}O + 2KBr$$

The *ethene monacetate* thus formed is a colourless liquid boiling at 182°, smelling slightly of acetic acid, and soluble in water. To convert it into the glycol the requisite quantity of powdered caustic potash or baryta is added, and the mixture distilled after standing for 12 hours.

Ethene alcohol has also been prepared by the action of moist silver oxide on ethene chloriodide. It is a thick colourless liquid, dissolving in water in all proportions, and possessing a sweet taste. It boils at 197°·5, and has at 0° the specific gravity 1·125. Sodium dissolves in it, with the evolution of hydrogen and formation of *sodium ethenate* $C_2H_4\left\{\begin{matrix}OH\\ ONa\end{matrix}\right.$, a white crystalline mass which when heated with more sodium to 190° yields *disodium ethenate* $C_2H_4\left\{\begin{matrix}ONa\\ ONa\end{matrix}\right.$. By acting with ethyl iodide on these compounds the ethyl ethers of ethene are formed. *Ethyl ethenate* $C_2H_4\left\{\begin{matrix}OH\\ OC_2H_5\end{matrix}\right.$ is a liquid possessing an ethereal odour and boiling at 127°·5, and *diethyl ethenate* $C_2H_4\left\{\begin{matrix}OC_2H_5\\ OC_2H_5\end{matrix}\right.$ is a similar body boiling at 123°·5. When glycol is acted upon by phosphorus pentachloride it is converted into ethene dichloride, and on heating it with zinc chloride it yields acetaldehyde:—



$$\begin{array}{l}CH_2OH\\ |\\ CH_2OH\end{array} - H_2O = \begin{array}{l}CH_3\\ |\\ COH\end{array}$$

By the action of concentrated hydriodic acid it is reduced to ethyl iodide:—

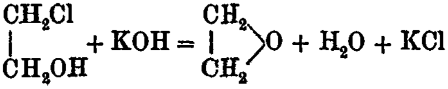
$$C_2H_4(OH)_2 + 3HI = C_2H_5I + 2H_2O + I_2$$

Ethene Chlorhydrate or Ethene Chlorhydrin $C_2H_4\left\{\begin{array}{l}Cl\\ OH\end{array}\right.$ is formed by shaking ethene with an aqueous solution of aqueous hypochlorous acid, or by heating glycol with hydrochloric acid:—

$$C_2H_4\left\{\begin{array}{l}OH\\ OH\end{array}\right. + \left.\begin{array}{l}Cl\\ H\end{array}\right\} = C_2H_4\left\{\begin{array}{l}Cl\\ OH\end{array}\right. + H_2O$$

It is a colourless liquid, miscible with water, and boiling at 128°. On heating it with potassium iodide it is converted into *ethene iodohydrate* $C_2H_4(OH)I$, a heavy liquid which is decomposed on heating. When sodium amalgam is added to an aqueous solution of ethene chlorhydrate, ethyl alcohol is formed. Oxidizing agents convert the chlorhydrate into monochloracetic acid.

Ethene Oxide C_2H_4O.—A solution of caustic potash acts violently on ethene chlorhydrate, ethene oxide being formed:—



$$\begin{array}{l}CH_2Cl\\ |\\ CH_2OH\end{array} + KOH = \begin{array}{l}CH_2\\ |\\ CH_2\end{array}\!\!>O + H_2O + KCl$$

Ethene oxide is a liquid boiling at 13°·5; it is miscible with water and has basic properties. Thus it combines readily with acids:—

$$C_2H_4O + HCl = C_2H_4\left\{\begin{array}{l}Cl\\ OH\end{array}\right.$$

$$C_2H_4O + \left.\begin{array}{r}C_2H_3O\\ H\end{array}\right\}O = C_2H_4\left\{\begin{array}{l}OH\\ OC_2H_3O\end{array}\right.$$

It precipitates also the solutions of many metallic salts, as those of magnesium, aluminium, copper, &c.:—

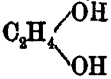
$$CuCl_2 + 2C_2H_4O = Cu(OH)_2 + 2C_2H_4\left\{\begin{array}{l}Cl\\ OH\end{array}\right.$$

When its aqueous solution is heated it combines with water, glycol being formed; it also combines with glycol, with the formation of diethene glycol:—

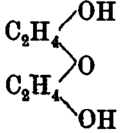
$$C_2H_4O + C_2H_4\left\{\begin{array}{l}OH\\ OH\end{array}\right. = \begin{array}{l}C_2H_4\\ \\ C_2H_4\end{array}\left|\begin{array}{l}OH\\ O\\ OH\end{array}\right.$$

Diethene glycol is a thick liquid, having a sweet taste and boiling at 250°. This compound may again be combined with ethene oxide, *triethene glycol* being produced, a liquid boiling at 287°. By repeating these reactions other poly-ethene glycols have been produced. The constitution of these compounds is shown by the following formulæ:—

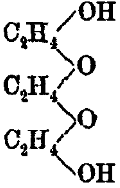
Ethene Glycol.



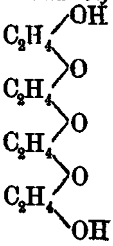
Diethene Glycol.



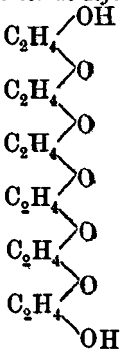
Triethene Glycol.



Tetra-ethene Glycol.

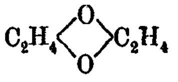


Hexethene Glycol.



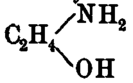
The same compounds are produced when ethene glycol is heated with ethene bromhydrate.

Nascent hydrogen converts ethene oxide into ethyl alcohol. It also combines with bromine, forming the compound $(C_2H_4O)_2Br_2$, consisting of reddish-brown crystals, melting at 65° and boiling at 95°. By adding mercury to this bromide *ethene dioxide* $(C_2H_4)_2O$ is obtained in colourless crystals, melting at 9° and boiling at 102°. The constitution of this compound is expressed by the formula:—

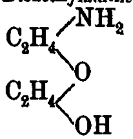


Ethene oxide unites also with ammonia and amines, forming strongly basic compounds. The hydrochlorides of these bases are also produced by combining ethene chlorhydrate with ammonia or compound ammonias. Ammonia yields the following bodies, which are all syrupy alkaline liquids, forming well-crystallized salts:—

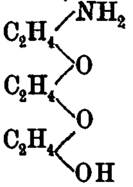
Monoxethylamine.



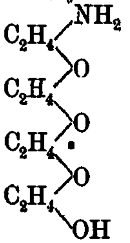
Dioxethylamine.



Trioxethylamine.



Tetroxethylamine.



Choline or Neurine $C_2H_4\left\{\begin{array}{l}OH\\ N(CH_3)_3OH\end{array}\right.$—This strong base was first discovered in the bile, and afterwards it was found in the brain, in the yolk of eggs, in mustard seed, &c. It does not exist in the free state in these substances, but is a product of decomposition of highly complicated compounds. Choline has also been produced synthetically by heating a concentrated aqueous solution of trimethylamine with ethene oxide:—

$$C_2H_4O + H_2O + N(CH_3)_3 = C_2H_4\left\{\begin{array}{l}OH\\ N(CH_3)_3OH\end{array}\right.$$

The free base is a deliquescent mass, having a strongly alkaline reaction, and readily absorbing carbon dioxide. It combines with acids to form crystalline salts. The platinum compound $(N[C_2H_4(OH)(CH_3)_3]Cl)_2 + PtCl_4$ forms large yellow plates, which dissolve in water, but are insoluble in alcohol.

When choline is heated it is resolved into glycol and trimethylamine:—

$$C_2H_4\left\{\begin{array}{l}OH\\ N(CH_3)_3OH\end{array}\right. = C_2H_4\left\{\begin{array}{l}OH\\ OH\end{array}\right. + N(CH_3)_3$$

Oxycholine or Betaïne $C_2H_2O\left\{\begin{array}{l}OH\\ N(CH_3)_3OH\end{array}\right.$—This base is obtained by the oxidation of choline, and by the action of trimethylamine upon monochloracetic acid:—

$$CH_2Cl.CO.OH + N(CH_3)_3 = N(CH_3)_3(CH_2.OH.CO)Cl$$

Oxycholine crystallizes from alcohol in large shining deliquescent crystals. It has no alkaline reaction and a sweetish and cooling taste; its salts crystallize well. Oxycholine occurs in beet-roots

(*Beta vulgaris*), and can easily be obtained in quantity from the treacle obtained in the manufacture of beet-root sugar.

Ethene Nitrite $C_2H_4(NO_2)_2$ is formed by passing ethene into liquid nitrogen tetroxide; it crystallizes in white prisms, melting at 37°·5 and subliming at a higher temperature with partial decomposition.

Ethene Nitrate $C_2H_4(NO_3)_2$.—When ethene glycol is dissolved in fuming nitric acid, much heat is evolved, and, on addition of water, ethene nitrate is precipitated as a thick, heavy oil, possessing an unpleasant, sweetish taste. On heating it gently it decomposes with a slight explosion, giving off a very luminous flame.

Ethene Chloronitrate $C_2H_4\left\{\begin{matrix}Cl\\NO_3\end{matrix}\right.$ is an oily, limpid, volatile liquid, having a pungent smell, and burning with a brilliant white flame. It is readily obtained by dissolving ethene chlorhydrate in concentrated nitric acid.

On passing ethene into a very cold mixture of concentrated nitric and sulphuric acids, the compound $C_2H_4N_2O_5$ or $C_2H_4\left\{\begin{matrix}NO_2\\NO_3\end{matrix}\right.$ is formed, a colourless oil, having a very pungent smell; its vapours attack the eyes and produce headache. By the action of aqueous hydriodic acid it is converted into glycol:—

$$C_2H_4\left\{\begin{matrix}NO_2\\NO_3\end{matrix}\right. + 4HI = C_2H_4\left\{\begin{matrix}OH\\OH\end{matrix}\right. + 2NO + 2I_2 + H_2O$$

Ethenesulphuric Acid $C_2H_4\left\{\begin{matrix}OH\\SO_4H\end{matrix}\right.$ is formed by heating glycol with sulphuric acid to 150°. On diluting the cold solution with water and neutralizing it with barium carbonate, *barium ethenesulphate* $\left.\begin{matrix}C_2H_4\left\{\begin{matrix}OH\\SO_4\end{matrix}\right.\\C_2H_4\left\{\begin{matrix}SO_4\\OH\end{matrix}\right.\end{matrix}\right\}Ba$ is obtained, a very soluble salt, which does not crystallize well. When it is heated with baryta-water it is decomposed into glycol and barium sulphate.

Carbyl Sulphate $C_2H_4(SO_3)_2$.—This name has been given to a compound which is produced by passing ethene into sulphur trioxide. It forms colourless crystals, which attract water rapidly from the air, being converted into *ethionic acid* $C_2H_4\left\{\begin{matrix}SO_4H\\SO_3H\end{matrix}\right.$, a compound only known in aqueous solution. On heating, it is decomposed into sulphuric acid and *isethionic* or *ethenesulphonic acid* $C_2H_4\left\{\begin{matrix}OH\\SO_3H\end{matrix}\right.$, which is also formed by diluting a saturated solution of sulphur trioxide in alcohol or ether with water and boiling the liquid for some hours. *Barium isethoniate* crystallizes from water in shining plates. By adding sulphuric acid to a solution of this salt, and boiling the filtrate down to the consistency of a syrup, *ethenesulphonic acid* crystallizes on cooling in white deliquescent needles. Potassium isethoniate is formed by heating ethene chlorhydrate with an aqueous solution of potassium sulphite :—

$$C_2H_4\left\{\begin{matrix}OH\\Cl\end{matrix}\right. + SO_3K_2 = C_2H_4\left\{\begin{matrix}OH\\SO_3K\end{matrix}\right. + ClK$$

Ammonium Isethoniate $C_2H_4\left\{\begin{matrix}OH\\SO_3NH_4\end{matrix}\right.$ crystallizes in colourless prisms, which when heated above 200° are converted into *amidoethylsulphonic acid* or *taurine* $C_2H_4\left\{\begin{matrix}NH_2\\SO_3H\end{matrix}\right.$, a compound which occurs in the free state and combined with cholic acid (taurocholic acid) in the bile, in the intestinal liquid, and in the lungs. It is best prepared from the bile of the ox, by boiling it for some time with hydrochloric acid and evaporating the filtered solution. The residue is exhausted with alcohol and the solution evaporated to crystallization. Taurine crystallizes in large colourless prisms, which are tasteless and only sparingly soluble in water. It is a monobasic acid and very stable body, which is not acted upon by boiling nitric acid; but nitrous acid converts it into isethonic acid :—

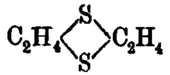
$$C_2H_4\left\{\begin{matrix}NH_2\\SO_3H\end{matrix}\right. + NO_2H = C_2H_4\left\{\begin{matrix}OH\\SO_3H\end{matrix}\right. + H_2O + N_2$$

On distilling potassium isethoniate with phosphorus pentachloride *isethonic chloride* $C_2H_4\left\{\begin{matrix}Cl\\SO_2Cl\end{matrix}\right.$ is obtained, which is decomposed by water with the formation of hydrochloric acid and *chlorethylsulphonic acid*, $C_2H_4\left\{\begin{matrix}Cl\\SO_2.OH.\end{matrix}\right.$ By acting with aqueous ammonia on the silver salt of this acid taurine is formed.

Ethene Dihydrosulphide or Ethene Mercaptan $C_2H_4\left\{\begin{matrix}SH\\SH\end{matrix}\right.$ is prepared by distilling ethene dibromide with an alcoholic solution of potassium hydrosulphide. It is a limpid, very refractive liquid, boiling at 142°, possessing a strong, disagreeable smell, and forming, like other mercaptans, metallic compounds.

Ethene Hydroxysulphide $C_2H_4\left\{\begin{matrix}OH\\OS\end{matrix}\right.$ is a liquid with similar properties. It is produced by the action of ethene chlorhydrate upon potassium hydrosulphide, and yields on oxidation isethonic acid.

Ethene Sulphide $(C_2H_4)_2S_2$ is obtained by distilling ethene bromide with an alcoholic solution of potassium sulphide. It is a crystalline solid, melting at 111° and boiling at 200°, but subliming readily at a lower temperature. The vapour density of this compound is 60 ($H = 1$), from which it follows that the molecular formula is twice C_2H_4S; its constitution must therefore be the following:—



Ethene Sulphocyanate $C_2H_4\begin{cases}SCN\\SCN\end{cases}$ is a white solid, crystallizing in plates. It is produced by heating ethene bromide with potassium sulphocyanate.

Ethenedisulphonic Acid $C_2H_4\begin{cases}SO_3H\\SO_3H\end{cases}$.—This bibasic acid is formed by oxidizing the sulphide, hydrosulphide, or sulphocyanate of ethene with strong nitric acid. It is also produced by heating ethene dibromide with potassium sulphite. It is a crystalline solid, which is very soluble in water, and has a very sour taste. The barium salt crystallizes in hexagonal plates, and is not decomposed by boiling nitric acid.

NITROGEN BASES OF ETHENE.

These compounds are formed by the action of ethene dibromide on alcoholic ammonia, the following reactions taking place :—

$$C_2H_4Br_2 + 2NH_3 = N_2\begin{cases}C_2H_4\\H_2\\H_2\end{cases} + 2HBr$$

$$2C_2H_4Br_2 + 4NH_3 = N_2\begin{cases}C_2H_4\\C_2H_4\\H_2\end{cases} + 2HBr + 2NH_4Br$$

$$3C_2H_4Br_2 + 6NH_3 = N_2\begin{cases}C_2H_4\\C_2H_4\\C_2H_4\end{cases} + 2HBr + 4NH_4Br$$

By adding caustic potash to the hydrobromides thus formed the bases are set free, and may be separated by fractional distillation.

Ethenediamine $C_2H_4(NH_2)_2$ is a strongly alkaline liquid, possessing an ammoniacal smell and caustic taste, and boiling at 123°. Nitrogen trioxide converts it into ethene oxide :—

$$C_2H_4(NH_2)_2 + N_2O_3 = C_2H_4O + 2H_2O + 2N_2$$

The hydrochloride of this base has been obtained in quantity by heating the impure ethene dichloride, obtained in the manufacture of chloral, with an excess of alcoholic ammonia for ten hours to 110°. The product is distilled in order to remove alcohol, dichlorethane and other chlorides, and the residue recrystallized from water.

By acting on ethenediamine with ethyl iodide the hydrogen of the amido-groups is replaced by ethyl, the final product being *hexethylethenediammonium di-iodide* $N_2(C_2H_4)(C_2H_5)_6I_2$, which when treated with silver oxide and water yields the corresponding hydroxide, a strongly alkaline and caustic substance.

Diethenediamine $(C_2H_4)_2N_2H_2$ boils at 170°, and combines, like ethenediamine, with two equivalents of an acid, forming crystallized salts. The two hydrogen atoms in the groups NH can also be replaced by alcohol radicals.

Triethenediamine $(C_2H_4)_3N_2$ boils at 210°, and combines with ethene dibromide to form *tetrethene-ammonium dibromide* $N_2(C_2H_4)_4Br_2$.

The triamines of the monad alcohol radicals act upon ethene dibromide in a peculiar manner. Thus trimethylamine and ethene dibromide readily combine, and form *monobromethyl-trimethylammonium bromide* $C_2H_4Br(CH_3)_3NBr$; nascent hydrogen converts this compound into ethyl-trimethylammonium bromide $C_2H_5(CH_3)_3NBr$, and by the action of moist silver oxide it yields choline:—

$$C_2H_4Br(CH_3)_3NBr + Ag_2 + H_2O = \left.\begin{matrix} C_2H_4(OH)(CH_3)_3N \\ H \end{matrix}\right\}O + 2AgBr$$

PHOSPHORUS- AND ARSENIC-BASES OF ETHENE.

Triethylphosphine combines with ethene dibromide, forming two compounds according to the relative quantities of the two constituents:—

Triethyl-bromethylphosphonium bromide $C_2H_4Br(C_2H_5)_3PBr$.

Hexethyl-ethenediphosphonium dibromide $C_2H_4\left\{\begin{matrix}(C_2H_5)_3P \\ (C_2H_5)_3P\end{matrix}\right\}Br_2$.

The monobromide crystallizes in regular dodecahedrons; on heating its aqueous solution with silver chloride it yields the compound $C_2H_4Br(C_2H_5)_3PCl$, but by acting on it with moist silver oxide all the bromine is replaced by hydroxyl, and the ammonium base $\left.\begin{matrix}C_2H_4(OH)(C_2H_5)_3P \\ H\end{matrix}\right\}O$ is formed, the constitution of which is analogous to that of choline.

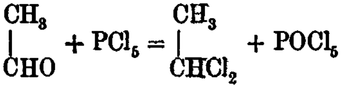
The second bromide corresponds to the compounds formed by uniting ethenediamine with the iodides of monad alcohol radicals.

Triethylarsine acts upon ethene dibromide in a similar manner as the phosphorus-base.

ETHIDENE COMPOUNDS.

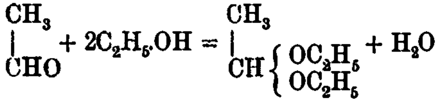
The radical ethidene $\begin{matrix}CH_3\\|\\CH\end{matrix}$ which is isomeric with ethene, does not exist in the free state; its oxide is acetaldehyde $\begin{matrix}CH_3\\|\\CHO\end{matrix}$

Ethidene Dichloride $C_2H_4Cl_2$ is identical with dichlorethane, and is formed by the action of chlorine upon ethyl chloride as well as by distilling aldehyde with phosphorus pentachloride. It boils at 58°.



$$\begin{matrix}CH_3\\|\\CHO\end{matrix} + PCl_5 = \begin{matrix}CH_3\\|\\CHCl_2\end{matrix} + POCl_3$$

Acetal $C_2H_4(OC_2H_5)$.—This isomeride of diethyl ethenate is obtained as a by-product in the preparation of aldehyde, and is also formed by heating aldehyde with alcohol to 100° in sealed tubes:—



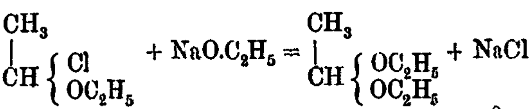
$$\begin{matrix}CH_3\\|\\CHO\end{matrix} + 2C_2H_5.OH = \begin{matrix}CH_3\\|\\CH\left\{\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix}\right.\end{matrix} + H_2O$$

or by the action of sodium ethylate upon ethidene dichloride. Acetal is a limpid liquid, possessing a refreshing odour, and boiling at 104°. On oxidation it yields aldehyde and acetic acid, and by heating it with acetic acid, ethyl acetate, aldehyde, and water are formed.

When a mixture of methyl alcohol and ethyl alcohol is oxidized by manganese dioxide and dilute sulphuric acid, a number of products are formed, among which are found *methyl-ethyl acetal* $C_2H_4\left\{\begin{matrix}OCH_3\\OC_2H_5\end{matrix}\right.$, boiling at 85°, and *dimethyl acetal* $C_2H_4\left\{\begin{matrix}OCH_3\\OCH_3\end{matrix}\right.$, boiling at 65°. The latter compound exists also in crude wood-spirit.

By distilling methyl alcohol with the above oxidizing mixture, it yields methyl formate and a liquid called *methylal* $C_3H_8O_2$, boiling at 42°, and possessing an agreeable odour. This body has most probably the constitution $CH_2(OCH_3)_2$, standing in the same relation to formaldehyde as acetal to acetaldehyde.

Aldehyde combines with ethyl chloride, forming the compound $C_2H_4\left\{\begin{matrix}Cl\\OC_2H_5\end{matrix}\right.$, a liquid boiling with decomposition at about 100°, and yielding acetal by the action of sodium ethylate:—



$$\begin{matrix}CH_3\\|\\CH\left\{\begin{matrix}Cl\\OC_2H_5\end{matrix}\right.\end{matrix} + NaO.C_2H_5 = \begin{matrix}CH_3\\|\\CH\left\{\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix}\right.\end{matrix} + NaCl$$

When aldehyde is heated with acetic anhydride to 180°, combination takes place, and *ethidene diacetate* is produced:—

$$CH_3.CHO + O\left\{\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\right. = CH_3.CH\left\{\begin{matrix}OC_2H_3O\\OC_2H_3O\end{matrix}\right.$$

This compound is an oily liquid, boiling at 169°, and possessing an alliaceous odour.

The compounds formed by the union of chloral with water and alcohols (page 146) have to be regarded as compounds of trichlorethidene:—

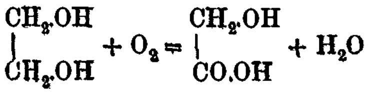
Chloral Hydrate or Trichlorethidene Alcohol.	Chloral Alcoholate.
$CCl_3.CH\left\{\begin{matrix}OH\\OH\end{matrix}\right.$	$CCl_3.CH\left\{\begin{matrix}OH\\OC_2H_5\end{matrix}\right.$

By treating chloral alcoholate with phosphorus pentachloride the hydroxyl is replaced by chlorine, and tetrachlorethyl oxide $\left.\begin{matrix}C_2HCl_4\\C_2H_5\end{matrix}\right\}O$ is formed (see page 112).

GLYCOLLYL COMPOUNDS.

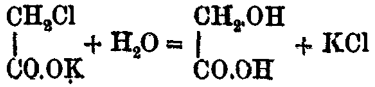
GLYCOLLIC ACID OR OXACETIC ACID $C_2H_4O_3$.

This acid can be produced by different reactions. It is formed by oxidizing glycol with weak nitric acid:—



$$\begin{matrix}CH_2.OH\\|\\CH_2.OH\end{matrix} + O_2 = \begin{matrix}CH_2.OH\\|\\CO.OH\end{matrix} + H_2O$$

and also by heating metallic chloracetates or bromacetates with water:—

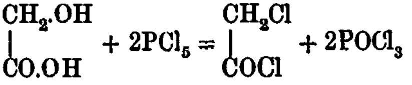


$$\begin{matrix}CH_2Cl\\|\\CO.OK\end{matrix} + H_2O = \begin{matrix}CH_2.OH\\|\\CO.OH\end{matrix} + KCl$$

Glycollic acid is, however, more conveniently prepared by oxidizing ethyl alcohol with nitric acid. One volume of nitric acid (1·33 specific gravity) is mixed with two volumes of alcohol (90 per cent.); after standing for some time evolution of gas commences. The liquid is now kept at a temperature of 20° until this evolution ceases, and then evaporated on a water-bath to the consistency of a syrup. The residue is dissolved in water, and the boiling solution neutralized with chalk. On cooling, impure calcium glycollate crystallizes out, which is boiled with milk of lime in order to remove by-products (glyoxal and glyoxylic acid). To obtain the pure acid the solution of the calcium salt is precipitated with oxalic acid, filtered, and the filtrate neutralized with lead carbonate. The lead salt thus obtained is crystallized, and the pure salt dissolved in water. Sulphuric acid is then added, but not sufficient to decompose all the lead glycollate, the solution evaporated to dryness, and the residue exhausted with ether. On evaporating the ether, glycollic acid crystallizes out, forming, when quite pure, large regular crystals which are very soluble in water, deliquesce in moist air, and melt at 79°. Glycollic acid exists in the juice of unripe grapes, and in the green leaves of the Virginia-creeper (*Ampelopsis hederacea*).

Calcium Glycollate $(C_2H_3O_3)_2Ca$ is sparingly soluble in cold water, and crystallizes from a hot saturated solution in colourless needles usually grouped in stars. By adding silver nitrate to its solution a white crystalline precipitate of silver glycollate is formed. Copper glycollate is a greenish-blue crystalline powder, which is obtained by mixing a solution of copper sulphate with a hot concentrated solution of the calcium salt.

Glycollyl Chloride $C_2H_2OCl_2$ is obtained by the action of phosphorus pentachloride on the acid; it is identical with monochloracetyl chloride, and yields with water monochloracetic acid. The formation of the chloride is explained by the equation :—

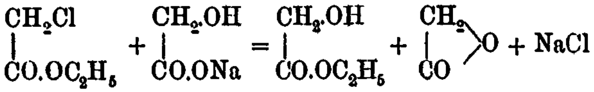


$$\begin{array}{l} CH_2.OH \\ | \\ CO.OH \end{array} + 2PCl_5 = \begin{array}{l} CH_2Cl \\ | \\ COCl \end{array} + 2POCl_3$$

GLYCOLLIC ETHERS.

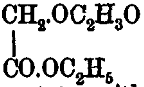
Ethylglycollic Acid $CH_2(OC_2H_5)CO.OH$ is produced by the action of sodium ethylate upon sodium monochloracetate. To prepare the free acid the copper-salt is decomposed by hydrogen sulphide. It is a thick, colourless liquid, boiling at about 200°, and having a very sour taste like glycollic acid.

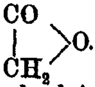
Ethyl Glycollate $CH_2(OH)CO.OC_2H_5$, a neutral liquid, soluble in water, is obtained, together with glycollic anhydride, by heating ethyl monochloracetate with sodium glycollate:—



$$\begin{array}{l} CH_2Cl \\ | \\ CO.OC_2H_5 \end{array} + \begin{array}{l} CH_2.OH \\ | \\ CO.ONa \end{array} = \begin{array}{l} CH_2.OH \\ | \\ CO.OC_2H_5 \end{array} + \left.\begin{array}{l} CH_2 \\ | \\ CO \end{array}\right>O + NaCl$$

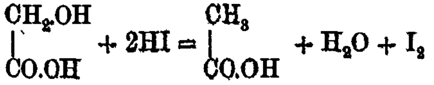
Diethyl Glycollate $CH_2(OC_2H_5)CO.OC_2H_5$ is conveniently prepared by dissolving sodium in absolute alcohol, and mixing this solution gradually with ethyl monochloracetate; the mixture is heated for some time, and the ether separated from the alcohol by fractional distillation. It is a colourless liquid, boiling at 155°, and possessing a sweetish taste.

Ethyl Acetylglycollate  $\begin{array}{l}CH_2.OC_2H_3O\\ |\\ CO.OC_2H_5\end{array}$.—This ether is obtained by heating ethyl monochloracetate with potassium acetate. It is a colourless liquid, having a pleasant fruity smell, and boiling at 179°. On distilling it with caustic potash it is resolved into potassium glycollate and acetic ether. When its aqueous solution is evaporated with slacked lime *in vacuo*, calcium acetate, calcium glycollate, and *calcium acetylglycollate* are produced: the latter salt crystallizes in small prisms.

Glycollide or Glycollic Anhydride  $\begin{array}{l}CO\\ |\\ CH_2\end{array}\!\!>O$.—When glycollic acid is heated above 150°, it is partially resolved into water and glycollide. The latter compound is formed in larger quantity when potassium monochloracetate is heated to 120°. It is a white amorphous powder. When heated with water it is slowly reconverted into glycollic acid; this change takes place more quickly in the presence of an alkali.

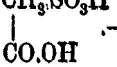
Diglycollic Acid or Paramalic Acid.—$O\left\{\begin{array}{l}CH_2.CO.OH\\ CH_2.CO.OH\end{array}\right.$.—This bibasic acid is formed by the oxidation of diethene glycol as well as by the dehydration of glycollic acid. It is also produced together with glycollic acid when monochloracetic acid is boiled with milk of lime and calcium chloride. It forms large monoclinic crystals, and is very soluble in water. When it is heated with fuming hydriodic acid it splits up into acetic acid and glycollic acid, and if the hydriodic acid be in excess the glycollic acid is also reduced to acetic acid:—

$$(1)\quad O\left\{\begin{array}{l}CH_2.CO.OH\\ CH_2.CO.OH\end{array}\right. + 2HI = HO.CH_2.CO.OH + CH_3.CO.OH + I_2$$

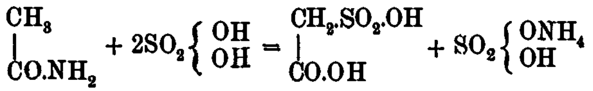
(2) 

$$\begin{array}{l}CH_2.OH\\ |\\ CO.OH\end{array} + 2HI = \begin{array}{l}CH_3\\ |\\ CO.OH\end{array} + H_2O + I_2$$

Diglycollic acid is metameric with malic acid.

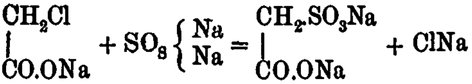
Sulphacetic Acid  $\begin{array}{l}CH_2.SO_3H\\ |\\ CO.OH\end{array}$.—This acid is obtained by heating a mixture of glacial acetic acid, and sulphur trioxide for some time, diluting with water and neutralizing with lead carbonate. The acid prepared from the lead salt by hydrogen sulphide crystallizes in transparent prisms; it is readily soluble in water and a strong bibasic acid.

It is also produced by the action of fuming sulphuric acid upon acetonitrile or acetamide:—



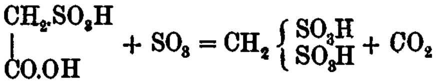
$$\begin{array}{l}CH_3\\ |\\ CO.NH_2\end{array} + 2SO_2\left\{\begin{array}{l}OH\\ OH\end{array}\right. = \begin{array}{l}CH_2.SO_2.OH\\ |\\ CO.OH\end{array} + SO_2\left\{\begin{array}{l}ONH_4\\ OH\end{array}\right.$$

and its sodium salt has also been obtained by boiling a solution of sodium sulphite with sodium monochloracetate:—



$$\begin{array}{l}CH_2Cl\\ |\\ CO.ONa\end{array} + SO_3\left\{\begin{array}{l}Na\\ Na\end{array}\right. = \begin{array}{l}CH_2.SO_3Na\\ |\\ CO.ONa\end{array} + ClNa$$

When sulphacetic acid is heated with sulphur trioxide it is converted into *methionic acid* or *methenedisulphonic acid*:—



$$\begin{array}{l}CH_2.SO_3H\\ |\\ CO.OH\end{array} + SO_3 = CH_2\left\{\begin{array}{l}SO_3H\\ SO_3H\end{array}\right. + CO_2$$

This acid is of course also formed when acetamide or acetonitrile are heated with a large excess of fuming sulphuric acid.

Methionic acid is the lower homologue of ethenedisulphonic acid (see Ethene Compounds), and is the second member of a series of sulphonic acids, which may be considered as substitution-products of marsh-gas, the first being *methylsulphonic acid* $CH_3.SO_3H$, a compound formed by the oxidation of methyl mercaptane, and the third is *methenyltrisulphonic acid*, a compound already described (see page 103):—

Methylsulphonic Acid.	Methenedisulphonic Acid.	Methenyltrisulphonic Acid.
$CH_3.SO_3H$	$CH_2(SO_3H)_2$	$CH(SO_3H)_3$

GLYCOLLIC AMIDES.

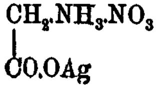
Glycollamide $\begin{array}{l}CH_2.OH\\ |\\ CO.NH_2\end{array}$ is produced by the action of dry ammonia upon glycollide or ethyl glycollate. It is soluble in water, crystallizing in colourless crystals with a slightly sweet taste. It forms very unstable salts.

Glycocol or Amidacetic Acid $\begin{array}{l}CH_2.NH_2\\ |\\ CO{\cdot}OH\end{array}$.—This compound, also called *glycocine*, is formed by heating monochlor- or monobromacetic acid with ammonia. It is a product of decomposition of glycocholic and hippuric acids, and is also produced when glue is boiled with dilute sulphuric acid. It forms large transparent crystals, possessing a sweet taste. It is a weak acid, the copper-salt being the most characteristic.

It is obtained by dissolving copper hydroxide in a boiling solution of glycocol; on cooling the salt crystallizes in fine, dark blue needles $[CH_2(NH_2)CO_2]_2Cu + H_2O$. *Silver amidacetate* $CH_2(NH_2)CO_2Ag$ separates from a hot solution in colourless crystals.

Glycocol is an acid, but at the same time also an amine, and combines therefore with acids.

Glycocol Hydrochloride $C_2H_3O_2.NH_3Cl$ is very soluble in water, and crystallizes in prisms; with platinic chloride it forms the double salt $2(C_2H_3O_2.NH_3Cl) + PtCl_4$, which is soluble in water and alcohol. Glycocol also combines with several salts as silver nitrate, &c. &c.:—



$$\begin{array}{l} CH_2.NH_3.NO_3 \\ | \\ CO.OAg \end{array}$$

When glycocol is heated with caustic baryta it is resolved into methylamine and carbon dioxide:—

$$CH_2(NH_2)CO_2H = CH_3.NH_2 + CO_2$$

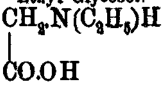
Nitrous acid converts it into glycollic acid:—

$$CH_2(NH_2)CO_2 + NO.OH = CH_2(OH)CO_2H + H_2O + N_2$$

Methyl-glycocol or Sarcosine $\begin{array}{l} CH_2.NH(CH_3) \\ | \\ CO.OH \end{array}$.—This compound was first obtained by boiling creatine with baryta-water (see Creatine), and can easily be obtained by acting with methylamine upon monochloracetic acid. It forms colourless crystals possessing a burning sweet taste; when heated it melts, and sublimes without decomposition. It combines with acids; the most characteristic of its salts is the platinum double compound $2[C_2H_3O_2.N(CH_3)H_2Cl] + PtCl_4$, which crystallizes in large pale-yellow octahedrons.

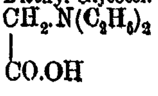
Similar compounds are formed by the action of ethylamine and diethylamine upon monochloracetic acid:—

Ethyl Glycocol.

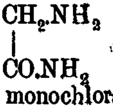


$$\begin{array}{l} CH_2.N(C_2H_5)H \\ | \\ CO.OH \end{array}$$

Diethyl-Glycocol.



$$\begin{array}{l} CH_2.N(C_2H_5)_2 \\ | \\ CO.OH \end{array}$$

Glycollyldiamide  $\begin{array}{l} CH_2.NH_2 \\ | \\ CO.NH_2 \end{array}$.—This compound is produced, but not readily, by heating monochloracetic acid or glycocol with a solution of ammonia in absolute alcohol. It is a crystalline, deliquescent mass, having an alkaline reaction; it combines readily with carbon dioxide, and with acids, forming crystalline salts. On boiling its aqueous solution it yields glycocol and ammonia.

OXALYL COMPOUNDS.

OXALIC ACID $C_2O_2(OH)_2$.

This important compound exists in many plants (Oxalis, Rumex, and Rheum species), as potassium or calcium salt. Its sodium-salt is obtained synthetically by passing carbon dioxide over sodium heated to 360°:—

$$2CO_2 + Na_2 = C_2O_4Na_2$$

The same salt is produced by the action of a high temperature upon sodium formate:—

$$\begin{array}{l} HCO.ONa \\ HCO.ONa \end{array} = \begin{array}{l} CO.ONa \\ | \\ CO.ONa \end{array} + H_2$$

Oxalic acid is an oxidation-product of glycol and glycollic acid; but also many other compounds, belonging to the group of fatty substances, yield oxalic acid as the final product of the action of nitric acid. Many of these bodies are also converted into oxalic acid by fusing them with caustic potash.

Acetic acid is oxidized to oxalic acid by heating it with a strongly alkaline solution of potassium permanganate.

Pure oxalic acid is best obtained by heating one part of cane-sugar with eight parts of nitric acid as long as red fumes are given off. The acid, crystallizing out on cooling, is purified by recrystallization from boiling water.

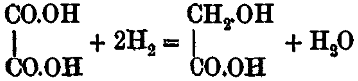
Commercial oxalic acid is produced by fusing saw-dust with a mixture of caustic potash and soda in the proportion of one equivalent of the former to two of the latter. The solution of the mixed alkalis having been evaporated to about 1·35 specific gravity, saw-dust is introduced so as to form a thick paste, which is placed on iron plates in thin layers and gradually heated, the mass being kept constantly stirred. During this process water is in the first instance given off; the mass then swells up and disengages inflammable gases, consisting of hydrogen and hydrocarbons, an aromatic odour at the same time being evolved. After the temperature has been maintained at 200° for one or two hours, the whole of the woody fibre is decomposed and the mass is entirely soluble in water. It contains, however, only from 1—4 per cent. of oxalic acid and about 0·5 per cent. of formic acid. The mass is now exposed still longer to the same temperature, care being taken to avoid any charring, which would cause a loss of oxalic acid. When perfectly dry it contains the maximum quantity of oxalic acid, viz. 28—30 per cent. of $C_2O_4H_2 + 2H_2O$, but no acetic acid, and very little more formic acid than before. The product, which is a grey powder, is in the next place treated with water; in this sodium and potassium salts dissolve, whilst sodium oxalate is left behind. The supernatant liquid is drawn off and evaporated to dryness, and the residual mass heated in furnaces to destroy the organic matter, and recover the alkalis. The sodium oxalate is decomposed by boiling with milk of lime, and the resulting calcium oxalate decomposed by means of sulphuric acid, and the liquor decanted from the calcium sulphate evaporated to crystallization. From about two parts of saw-dust one part of crystallized oxalic acid is obtained. The commercial acid always contains a trace of alkali, which cannot be completely removed by recrystallization.

Oxalic acid crystallizes in colourless prisms $C_2H_2O_4 + 2H_2O$, which at 100° lose their water, and crumble down to a white powder. The crystallized acid dissolves in 8 parts of water at the common temperature, and in about its own weight of boiling water; it is also very soluble in spirits of wine. It has an intensely sour taste, and is very poisonous, the antidotes being chalk or magnesia.

The anhydrous acid sublimes when carefully heated; its vapours are very irritating. On heating the crystallized acid quickly it is resolved into carbon monoxide, carbon dioxide, water, and formic acid. Oxidizing agents convert it into water and carbon dioxide; this reaction is made use of in volumetric analysis to determine the strength of a solution of potassium permanganate:—

$$K_2Mn_2O_8 + 3H_2SO_4 + 5C_2O_4H_2 = K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2$$

By boiling oxalic acid with zinc and sulphuric acid it is reduced to glycollic acid:—



$$\begin{array}{l}CO.OH\\ |\\ CO.OH\end{array} + 2H_2 = \begin{array}{l}CH_2.OH\\ |\\ CO.OH\end{array} + H_2O$$

The hydroxyl of oxalic acid cannot be replaced by chlorine; by acting on it with phosphorus pentachloride, it is decomposed according to the equation:—

$$PCl_5 + C_2H_2O_4 = POCl_3 + 2HCl + CO + CO_2$$

OXALATES.

Oxalic acid is a powerful bibasic acid, decomposing dry sodium chloride when heated, with the evolution of hydrochloric acid, and converting sodium chloride or nitrate in solution into sodium binoxalate.

Potassium Oxalates.—The normal salt $C_2O_4K_2 + H_2O$ forms monoclinic crystals, and is readily soluble in water. The acid salt $C_2O_4HK + H_2O$ is less soluble, and possesses a sour taste; it occurs in several species of Rumex and Oxalis. It combines with oxalic acid, forming the so-called potassium quadroxalate C_2O_4HK

$+ C_2O_4H_2 + 2H_2O$, a salt sparingly soluble in water and crystallizing in large octahedrons. The two acid oxalates are known in commerce by the name of "salts of sorrel," or "salt of lemon."

Normal Sodium Oxalate C_2O_4Na is a white sandy powder, and only slightly soluble in cold water.

Ammonium Oxalate $C_2O_4(NH_4)_2 + H_2O$ crystallizes in rhombic prisms, and is used as a reagent for calcium salts.

Calcium Oxalate C_2O_4Ca occurs in the form of quadratic prisms, containing three molecules of water, in the cells of different plants (rhubarb-root, lichens, &c.), and in urine and other animal fluids.

It also forms the chief constituent of the urinary calculi called "mulberry stones." When a neutral solution of a calcium salt is mixed with that of an oxalate, a crystalline precipitate of calcium oxalate is formed, even in highly diluted solutions; it is insoluble in water and acetic acid, but readily dissolves in dilute nitric and hydrochloric acids.

Ferrous Oxalate C_2O_4Fe is obtained as a bright yellow precipitate by mixing solutions of oxalic acid and ferrous sulphate. *Ferric oxalate* $(C_2O_4)_3Fe_2$ is very soluble in water, and is readily formed by dissolving ferric hydroxide in a solution of oxalic acid.

The oxalates of lead, mercury, and silver are heavy white precipitates. The silver and mercury salts decompose with a sudden flash when heated, but on percussion the latter explodes violently.

ETHERS OF OXALIC ACID.

Methyl Oxalate $C_2O_4(CH_3)_2$.—The preparation of this ether has been already described (see Methyl Alcohol). It forms large rhombic crystals, melting at 51° and boiling at 162°. It is soluble in water, which decomposes it slowly in the cold, quickly on boiling, into methyl alcohol and oxalic acid.

Ethyl Oxalate $C_2O_4(C_2H_5)_2$ is produced by distilling absolute alcohol with anhydrous oxalic acid. It is a colourless liquid, boiling at 186°. Water, in which it is only sparingly soluble, acts on it in a similar manner as on the methyl-ether.

By acting on it with an alcoholic solution of caustic potash in the cold, *potassium ethyloxalate* $C_2O_4\left\{\begin{matrix}K\\C_2H_5\end{matrix}\right.$ separates in crystals. *Ethyl-oxalic acid* is also formed as a by-product in the preparation of ethyl oxalate. It is a very unstable compound, and scarcely known in the pure state; when it is heated it splits up into carbon dioxide and ethyl formate:—

$$\begin{matrix}CO.OC_2H_5\\ |\\ CO.OH\end{matrix} = CHO.OC_2H_5 + CO_2$$

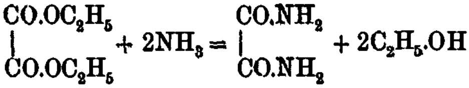
Phosphorus oxychloride acts violently upon potassium ethyloxalate, the *chloride of ethyloxalic acid* $C_2O_2\left\{\begin{array}{l}Cl\\OC_2H_5\end{array}\right.$ being formed, a limpid liquid, boiling at 140° and possessing a suffocating smell. It fumes in the air, and is acted upon by water and alcohol like other acid chlorides.

When sodium amalgam is added to a solution of ethyl oxalate in alcohol the oxalic acid is reduced to *glycollic acid* and *tartaric acid.* But when sodium amalgam acts upon dry ethyl oxalate, the reaction is different, the chief product consisting of *desoxalic acid*, a compound to be described further on.

Sodium or potassium dissolve in ethyl oxalate with the evolution of carbon dioxide, and the formation of a black mass, which on distillation yields ethyl carbonate, which compound was first discovered by this reaction. The same reaction takes place by acting on oxalic ether with sodium ethylate, which compound is always first formed by the action of the metal upon ethyl oxalate. Besides carbon dioxide and ethyl carbonate, other products also are formed in small quantity, such as ethyl alcohol, formic acid, &c.

AMIDES OF OXALIC ACID.

Oxamide $C_2O_2(NH_2)_2$ is obtained by the action of aqueous ammonia upon oxalic ether :—

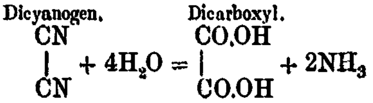


$$\begin{array}{l}CO.OC_2H_5\\|\\CO.OC_2H_5\end{array} + 2NH_3 = \begin{array}{l}CO.NH_2\\|\\CO.NH_2\end{array} + 2C_2H_5.OH$$

The same compound is produced when normal ammonium oxalate is heated :—

$$C_2O_2(ONH_4)_2 = C_2O_2(NH_2)_2 + 2H_2O$$

When cyanogen gas is passed into concentrated hydrochloric acid, or when aldehyde is added to an aqueous solution of cyanogen, it takes up water and is converted into oxamide. On the other hand, when oxamide is heated with phosphorus pentoxide it is resolved into water and cyanogen gas. These reactions show that dicyanogen is the nitrile of oxalic acid or *dicarboxyl* :—



$$\overset{\text{Dicyanogen.}}{\begin{array}{l}CN\\|\\CN\end{array}} + 4H_2O = \overset{\text{Dicarboxyl.}}{\begin{array}{l}CO.OH\\|\\CO.OH\end{array}} + 2NH_3$$

Oxamide is a white crystalline powder, which is but sparingly soluble in water and alcohol. When it is boiled with acids or alkalis it takes up water and yields oxalic acid and ammonia. On heating it with mercuric oxide it forms urea and carbon dioxide.

Oxamic Acid $C_2O_2\left\{\begin{matrix}OH\\NH_2\end{matrix}\right.$ is produced when acid ammonium oxalate is heated, and its ammonium salt is formed when oxamide is boiled with aqueous ammonia:—

$$C_2O_2\left\{\begin{matrix}NH_2\\NH_2\end{matrix}\right. + H_2O = C_2O_2\left\{\begin{matrix}NH_2\\ONH_4\end{matrix}\right.$$

Oxamic acid is a white crystalline powder, which is not very soluble in water. It is a monobasic acid, forming well-crystallized salts. By heating it with water it is reconverted into acid ammonium oxalate.

Ethyl Oxamate $C_2O_2\left\{\begin{matrix}NH_2\\OC_2H_5\end{matrix}\right.$.—This compound, also called *oxamethane*, is formed by evaporating a solution of ethyl oxalate in ammoniacal absolute alcohol, and is also produced by the action of dry ammonia upon the chloride of ethyloxalic acid. It crystallizes in pearly scales; aqueous ammonia decomposes it into oxamide and ethyl alcohol.

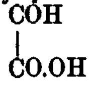
Ethyl-Oxamic Acid $C_2O_2\left\{\begin{matrix}NH.C_2H_5\\OH\end{matrix}\right.$ is metameric with the last compound, and is produced by heating acid oxalate of ethylamine to 180°. It sublimes in white interwoven needles, and is soluble in water and a strong monobasic acid.

Oxalohydroxamic Acid or Dihydroxyl-oxamide $C_2O_2\left\{\begin{matrix}NH.OH\\NH.OH\end{matrix}\right.$ is formed by heating an alcoholic solution of hydroxylamine with ethyl oxalate. It forms colourless crystals, and is very sparingly soluble in cold water. When heated to 103° it burns like gunpowder. The hydrogen in the two hydroxyls can be replaced by metals, crystalline salts being formed which explode on heating.

ALDEHYDES OF OXALIC ACID.

Both aldehydes of bibasic oxalic acid are known, viz.:—

Glyoxylic Acid.



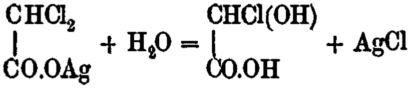
$$\begin{matrix}COH\\|\\CO.OH\end{matrix}$$

Glyoxal.

$$\begin{matrix}COH\\|\\COH\end{matrix}$$

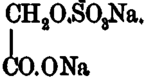
These compounds are produced, together with glycollic acid, when alcohol is oxidized with nitric acid.

Glyoxylic Acid is also produced on boiling oxalic acid with zinc and dilute sulphuric acid, and on heating dichloracetic acid with water and silver oxide. The latter reaction takes place in two stages. First *monochloroglycollic acid* is formed:—



$$\begin{matrix} CHCl_2 \\ | \\ CO.OAg \end{matrix} + H_2O = \begin{matrix} CHCl(OH) \\ | \\ CO.OH \end{matrix} + AgCl$$

and this compound is by the further action of silver oxide converted into glyoxylic acid. The free acid forms a sour, thick, syrupy liquid.



Glyoxylic acid is easily oxidized to oxalic acid, and like other aldehydes it combines with the sulphites of the alkali-metals forming crystalline compounds as $\begin{matrix} CH_2O.SO_3Na. \\ | \\ CO.ONa \end{matrix}$ When the acid is heated with an ammoniacal solution of silver nitrate, metallic silver separates out as a brilliant mirror:—

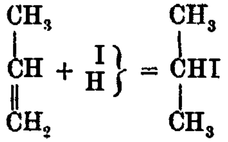
$$C_2H_4O_4 + Ag_2O = C_2H_2O_4 + H_2O + Ag_2$$

Glyoxal or Oxaldehyde $C_2H_2O_2$.—This compound is isolated from the crude calcium glycollate by treating it with alcohol, which dissolves the glyoxal whilst the calcium salts of glyoxylic and glycollic acids are left behind. On shaking the alcoholic solution with acid sodium sulphite a crystalline precipitate of glyoxal-sodium sulphite is formed, which with barium chloride yields the corresponding sparingly soluble barium salt. By decomposing this compound with dilute sulphuric acid, and evaporating the filtrate, glyoxal is left behind as a crystalline, deliquescent mass. By the action of weak nitric acid it yields glyoxylic acid, whilst a stronger acid oxidizes it to oxalic acid. Alkalis readily convert it into glycollic acid, even more easily than the isomeric glycollide (page 198).

PROPENE COMPOUNDS.

Propene or Propylene C_3H_6, a gas resembling ethene, is produced by heating propyl alcohol with concentrated sulphuric acid, or by the action of alcoholic potash solution upon secondary propyl iodide. Pure propene is also readily obtained by bringing allyl iodide C_3H_5I (see Allyl Compounds) in contact with zinc and dilute hydrochloric acid. When the vapours of amyl alcohol or isobutyl alcohol are passed through a red-hot tube, or when valerianic acid is heated with quicklime, the products of decomposition always contain a large proportion of propene. It also occurs in coal gas.

Propene is a colourless gas condensible to a liquid by strong pressure; it readily combines with hydriodic acid, forming secondary propyl iodide:—



$$\begin{array}{c}CH_3\\|\\CH\\\|\\CH_2\end{array} + \left.\begin{array}{c}I\\H\end{array}\right\} = \begin{array}{c}CH_3\\|\\CHI\\|\\CH_3\end{array}$$

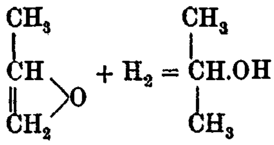
Propene Dichloride $C_3H_6Cl_2$, a colourless liquid smelling like ethene chloride, is produced by the direct union of propene and chlorine, as well as by the action of chlorine upon propane or propyl chloride. It boils at 96°.

Propene Dibromide $C_3H_6Br_2$ is a heavy colourless liquid boiling at 142°, which is generally used for preparing other propene compounds.

Propene Glycol $C_3H_6(OH)_2$ is obtained from propene dibromide by a reaction similar to that by which ethene dibromide is converted into ethene glycol.

It is a thick liquid having a sweet taste, and boiling at 188°. By the action of hydriodic acid it is reduced to secondary propyl iodide.

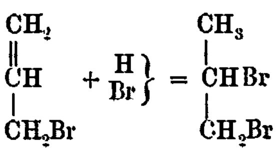
On heating a saturated solution of hydrochloric acid gas in propene glycol, *propene chlorhydrate* $C_3H_6\left\{\begin{array}{l}Cl\\OH\end{array}\right.$ is produced, a liquid boiling at 127°. By the action of caustic potash it is converted into *propene oxide* C_3H_6O, a liquid soluble in water and boiling at 35°. It combines with nascent hydrogen to form secondary propyl alcohol:—



$$\left.\begin{array}{c}CH_3\\|\\CH\\\|\\CH_2\end{array}\right>O + H_2 = \begin{array}{c}CH_3\\|\\CH.OH\\|\\CH_3\end{array}$$

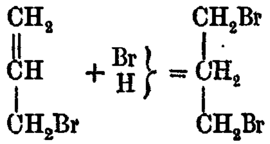
ISOMERIDES OF PROPENE COMPOUNDS.

Trimethene Dibromide $C_3H_6Br_2$.—When allyl bromide C_3H_5Br, a body belonging to the non-saturated compounds, is treated with hydrobromic acid, two isomeric dibromides are found. That which is obtained in a small quantity consists of common propene dibromide, formed according to the following reaction:—



$$\begin{array}{c}CH_2\\\|\\CH\\|\\CH_2Br\end{array} + \left.\begin{array}{c}H\\Br\end{array}\right\} = \begin{array}{c}CH_3\\|\\CHBr\\|\\CH_2Br\end{array}$$

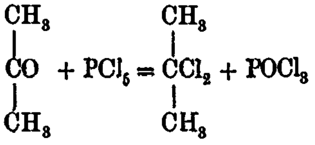
The second bromide, which is always present in a larger quantity, is trimethene dibromide:—



$$\begin{array}{l}CH_2\\ \|\\ CH\\ |\\ CH_2Br\end{array} + \left.\begin{array}{l}Br\\ H\end{array}\right\} = \begin{array}{l}CH_2Br\\ |\\ CH_2\\ |\\ CH_2Br\end{array}$$

Trimethene dibromide is a liquid boiling at 163°. On heating it with silver acetate and acetic acid it yields an acetate, which on distillation with caustic baryta is converted into *trimethene glycol* or *primary propene alcohol* $CH_2\left\{\begin{array}{l}CH_2.OH\\ CH_2.OH\end{array}\right.$ a thick liquid, possessing a sweet taste and boiling at about 212°.

Propidene Dichloride or Methylchloracetol $C_3H_6O_2$ is formed, together with the isomeric propene dichloride, by the action of chlorine upon propyl chloride. The pure compound is produced when dimethyl ketone is distilled with phosphorus pentachloride:—



$$\begin{array}{l}CH_3\\ |\\ CO\\ |\\ CH_3\end{array} + PCl_5 = \begin{array}{l}CH_3\\ |\\ CCl_2\\ |\\ CH_3\end{array} + POCl_3$$

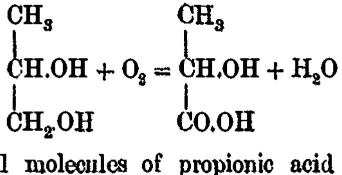
It is a colourless liquid boiling at 70°. By the action of sodium it is converted into common propene, and not, as might be expected, into an isomeride. On treating it with alcoholic potash it yields *monochloropropene* C_3H_5Cl, a compound which is also obtained by the same reaction from propene dichloride.

LACTYL COMPOUNDS.

LACTIC ACID OR *α* OXYPROPIONIC ACID $C_3H_6O_3$.

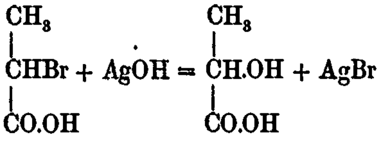
This acid can be produced artificially by several reactions:—

(1) By bringing propene glycol in contact with platinum-black in the presence of air:—



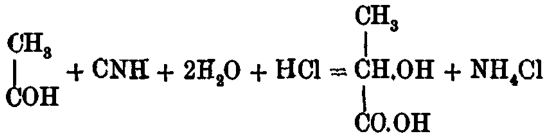
$$\begin{array}{l}CH_3\\ |\\ CH.OH\\ |\\ CH_2.OH\end{array} + O_2 = \begin{array}{l}CH_3\\ |\\ CH.OH\\ |\\ CO.OH\end{array} + H_2O$$

(2) When equal molecules of propionic acid and bromine are heated in sealed tubes to 150°, *α bromopropionic acid* is formed, which, when heated with water and silver oxide, is converted into *lactic acid*:—



$$\begin{array}{l}CH_3\\ |\\ CHBr\\ |\\ CO.OH\end{array} + AgOH = \begin{array}{l}CH_3\\ |\\ CH.OH\\ |\\ CO.OH\end{array} + AgBr$$

(3) Anhydrous prussic acid unites with aldehyde, forming the compound $C_2H_4O.CNH$, a liquid boiling with partial decomposition at 183°. Alkalis decompose it again into its constituents, but hydrochloric acid converts it into ammonium chloride and lactic acid:—



$$\begin{array}{l}CH_3\\ |\\ COH\end{array} + CNH + 2H_2O + HCl = \begin{array}{l}CH_3\\ |\\ CH.OH\\ |\\ CO.OH\end{array} + NH_4Cl$$

Lactic acid exists in the gastric juice and in Turkey opium, and it is also produced by the lactic fermentation of sugar, gum, and starch. It occurs therefore in sour milk, sour cabbage, in the fermented juice of beetroot, and in spent tan. It is also formed together with other products when grape-sugar is heated with a solution of caustic soda.

Lactic acid is easily obtained in quantity by the following process: 3 kilograms of cane-sugar and 15 grams of tartaric acid are dissolved in 17 litres of boiling water. After the solution has stood for a few days, 100 grams of putrid cheese and 1·2 kilograms of zinc-white, which have been mixed to a creamy liquid with 4 litres of sour milk, are added, and the mixture is exposed to a temperature of 30°—35° for eight or ten days. The product is heated to the boiling-point, filtered, and evaporated to crystallization. The zinc lactate thus obtained is purified by recrystallization from boiling water, then dissolved in water, decomposed by hydrogen sulphide, and the filtrate evaporated on a water-bath. The residue, consisting of impure lactic acid, is dissolved in a small quantity of water and the solution shaken with ether. On evaporating the ethereal solution pure aqueous lactic acid is obtained, forming a colourless, syrupy liquid, possessing a very sour taste.

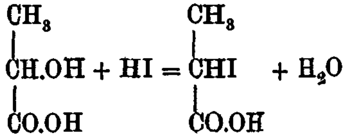
LACTATES.

The lactates of the alkali metals are very soluble in water, and do not crystallize.

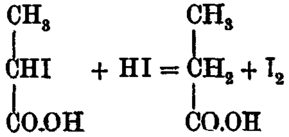
Calcium Lactate $(C_3H_5O_3)_2Ca + 5H_2O$ crystallizes from a hot aqueous solution in warty needles. *Zinc lactate* $(C_3H_5O)_2Zn + 3H_2O$ is the most characteristic salt of this acid; it crystallizes in shining four-sided prisms, and dissolves in six parts of boiling and fifty-eight parts of cold water; it is insoluble in alcohol. *Ferrous lactate* $(C_3H_5O_3)_2Fe$

+ $3H_2O$ is prepared by dissolving iron filings in sour whey. It forms nearly colourless crystalline crusts; it is but sparingly soluble in water, and is used in medicine.

When a mixture of lactic acid and phosphorus di-iodide P_2I_4 is introduced in water, *a iodopropionic acid* is formed, an oily liquid insoluble in water, which, when heated with strong hydriodic acid to 150°, is converted into propionic acid. This transformation of lactic acid into propionic acid is explained by the following equations:—

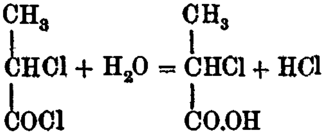
(1) 

$$\begin{array}{l} CH_3 \\ | \\ CH.OH \\ | \\ CO.OH \end{array} + HI = \begin{array}{l} CH_3 \\ | \\ CHI \\ | \\ CO.OH \end{array} + H_2O$$

(2) 

$$\begin{array}{l} CH_3 \\ | \\ CHI \\ | \\ CO.OH \end{array} + HI = \begin{array}{l} CH_3 \\ | \\ CH_2 \\ | \\ CO.OH \end{array} + I_2$$

Lactyl Chloride $C_3H_4OCl_2$.—This compound is obtained by distilling two molecules of phosphorus pentachloride with one molecule of calcium lactate. It is a fuming liquid, which has not been obtained quite free from phosphorus oxychloride. It is decomposed by cold water with the formation of hydrochloric acid and *a chloropropionic acid*, a colourless liquid, boiling at 186°.

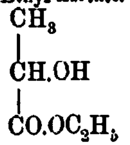


$$\begin{array}{l} CH_3 \\ | \\ CHCl \\ | \\ COCl \end{array} + H_2O = \begin{array}{l} CH_3 \\ | \\ CHCl \\ | \\ CO.OH \end{array} + HCl$$

ETHERS OF LACTIC ACID.

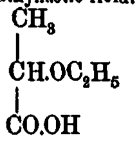
Ethyl Lactate, a colourless neutral liquid boiling at 156°, is produced by heating lactic acid with absolute alcohol. It is soluble in water; its aqueous solution soon turns acid, being decomposed into alcohol and lactic acid. Sodium dissolves in ethyl lactate with the evolution of hydrogen. On heating the sodium compound thus formed with ethyl iodide, diethyl lactate is formed, a liquid possessing an agreeable odour, and boiling, like the monolactate, at 156°. By the action of hot potash-solution it yields potassium ethyllactate; the free ethyllactic acid is as yet very little known. The constitution of these ethers is shown by the following formulæ:—

Ethyl Lactate.



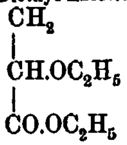
$$\begin{array}{l} CH_3 \\ | \\ CH.OH \\ | \\ CO.OC_2H_5 \end{array}$$

Ethyllactic Acid.



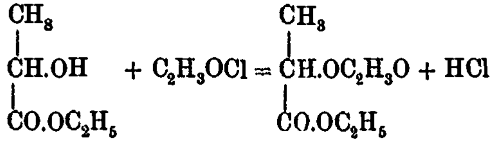
$$\begin{array}{l} CH_3 \\ | \\ CH.OC_2H_5 \\ | \\ CO.OH \end{array}$$

Diethyl Lactate.



$$\begin{array}{l} CH_2 \\ | \\ CH.OC_2H_5 \\ | \\ CO.OC_2H_5 \end{array}$$

Acetyllactic Acid or Lactyl Acetate $CH_3.CH(OC_2H_3O)CO_2H$.—When ethyl lactate is heated with acetyl chloride, the ethyl-ether of acetyl-lactic acid is formed:—



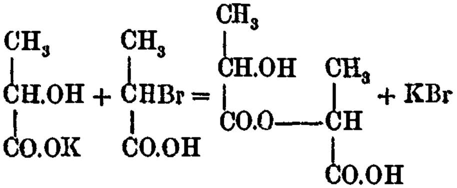
$$\begin{array}{l} CH_3 \\ | \\ CH.OH \\ | \\ CO.OC_2H_5 \end{array} + C_2H_3OCl = \begin{array}{l} CH_3 \\ | \\ CH.OC_2H_3O \\ | \\ CO.OC_2H_5 \end{array} + HCl$$

Ethyl acetyllactate is a liquid boiling at 177°, and possessing a fruity smell. On heating it with water for 2—3 hours to 150° it decomposes into alcohol and acetyllactic acid, a thick, very sour liquid.

Nitrolactic Acid or Lactyl Nitrate $CH_3.CH(ONO_2)CO_2H$ is produced by dissolving lactic acid in a mixture of concentrated nitric and sulphuric acids. It is a colourless, viscid liquid, possessing a very sour taste and a faint nitrous odour; in pure water it dissolves but sparingly, but readily in dilute acids. It is a very unstable compound, decomposing slowly at the ordinary temperature, and quickly on heating, with the evolution of nitrous fumes. Caustic alkalis quickly convert it into a nitrate and a lactate.

Ethyl Nitrolactate $CH_3.CH(ONO_2)CO_2.C_2H_5$.—To obtain this compound, ethyl lactate is dissolved in concentrated nitric acid; on adding sulphuric acid to this solution the ether separates out as an oily, limpid liquid, possessing an agreeable odour and pungent sweet taste. It boils with slight decomposition at 178°, and burns like nitrolactic acid with a brilliant flame.

Lactic Anhydride $C_{12}H_{10}O_5$.—When lactic acid is heated to 150°, water is formed, and a yellowish amorphous residue is obtained, which is commonly called lactic anhydride. The same compound is formed by heating potassium lactate with *a* bromopropionic acid. The latter reaction shows that this compound is an ether, containing two residues of lactic acid, one playing the part of an alcohol radical, and the other that of an acid radical:—

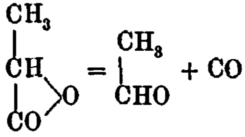


$$\begin{array}{l} CH_3 \\ | \\ CH.OH \\ | \\ CO.OK \end{array} + \begin{array}{l} CH_3 \\ | \\ CHBr \\ | \\ CO.OH \end{array} = \begin{array}{llll} CH_3 & & & \\ | & & & \\ CH.OH & & CH_3 & \\ | & & | & \\ CO.O & — & CH & \\ & & | & \\ & & CO.OH & \end{array} + KBr$$

This etherification also takes place slowly, when an aqueous solution of lactic acid is allowed to remain over sulphuric *in vacuo*, and for this reason pure anhydrous lactic acid is not obtainable.

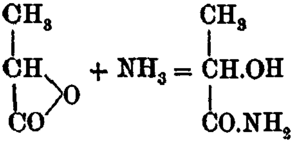
The anhydride is very slowly decomposed by water alone, but quickly in presence of alkalis, into two molecules of lactic acid.

Lactide $C_2H_4O_2$.—When the so-called anhydride is heated to 210°, lactide, or the real lactic anhydride, is formed. It crystallizes from alcohol in shining rhombic plates, and is sparingly soluble in water, with which it slowly combines, to form lactic acid. When quickly heated it splits up into carbon monoxide and aldehyde:—



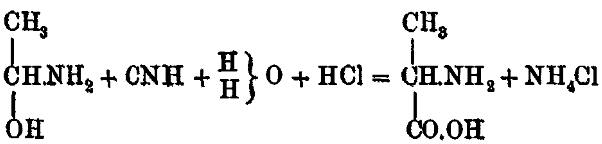
AMIDES OF LACTIC ACID.

Lactamide $C_2H_4(OH)CONH_2$ is formed by the combination of lactide with dry ammonia:—



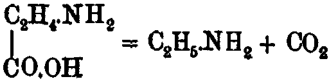
The same compound is produced by heating ethyl lactate with ammonia; it is freely soluble in water, and crystallizes in plates, melting at 74°. When it is heated with potash-solution, ammonia is evolved and potassium lactate is formed.

Alanine or Amidopropionic Acid $C_2H_4(NH_2)CO_2H$.—This compound is obtained by heating ethyl *a* chloropropionate with ammonia, or by boiling two parts of aldehyde-ammonia and one part of anhydrous prussic acid with an excess of dilute hydrochloric acid:—



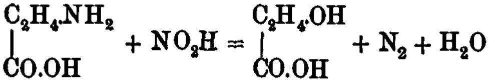
$$\begin{array}{l}CH_3\\ |\\ CH.NH_2\\ |\\ OH\end{array} + CNH + \left.\begin{array}{c}H\\ H\end{array}\right\}O + HCl = \begin{array}{l}CH_3\\ |\\ CH.NH_2\\ |\\ CO.OH\end{array} + NH_4Cl$$

On evaporating the solution a mixture of sal-ammoniac and alanine hydrochloride crystallizes out. The latter is dissolved in absolute alcohol, and the solution treated with lead hydroxide, lead chloride being formed and *lead amidopropionate*, which is decomposed with hydrogen sulphide. Alanine crystallizes from an alcoholic solution in shining prisms which are freely soluble in water, but sparingly in alcohol and insoluble in ether. Its solution has a neutral reaction and a sweet taste. On heating it carefully it sublimes, but when the temperature is raised quickly a large portion splits up into carbon dioxide and ethylamine:—



$$\begin{array}{l} C_2H_4.NH_2 \\ | \\ CO.OH \end{array} = C_2H_5.NH_2 + CO_2$$

Like glycocol it combines with acids, yielding soluble salts; it also forms, as acid, metallic salts. Nitrous acid acts on it as on other amido-compounds, lactic acid, nitrogen, and water being formed:—

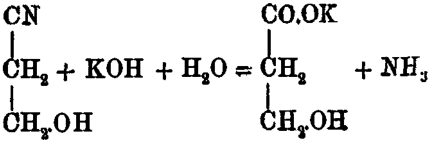


$$\begin{array}{l} C_2H_4.NH_2 \\ | \\ CO.OH \end{array} + NO_2H = \begin{array}{l} C_2H_4.OH \\ | \\ CO.OH \end{array} + N_2 + H_2O$$

Trichlorolactic Acid $CCl_3.CH\left\{\begin{array}{l} OH \\ CO.OH \end{array}\right.$.—When chloral is digested with aqueous hydrocyanic acid, they combine, forming the *nitrile* of trichlorolactic acid $CCl_3.CH\left\{\begin{array}{l} OH \\ CN \end{array}\right.$, a crystalline solid, which, by continued boiling with hydrochloric acid, is converted into trichlorolactic acid, a solid melting at 110°. Its salts readily split up on heating them with excess of base into a formate and chloral.

ETHENE-LACTYL AND MALONYL COMPOUNDS.

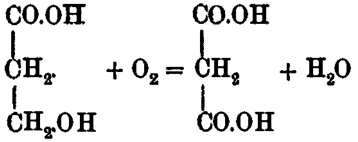
Sarcolactic Acid $C_3H_6O_3$.—This name is given to an acid occurring in the muscular flesh, from which it can be extracted by water, and is also found in different animal secretions. Recent researches have shown that this body is a mixture of two acids; one of these, called *paralactic acid*, has the greatest resemblance to common lactic acid, from which it only differs by being optically active. The second acid is called *ethene-lactic acid*, because it has been obtained synthetically from ethene compounds, just as common lactic acid is derived from ethidene compounds (aldehyde). By heating ethene chlorhydrate with potassium cyanide the nitrile of ethene-lactic acid is formed, which, on boiling with caustic potash, yields the potassium salt of this acid:—



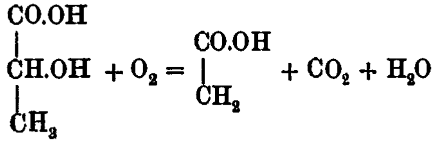
$$\begin{array}{l} CN \\ | \\ CH_2 \\ | \\ CH_2.OH \end{array} + KOH + H_2O = \begin{array}{l} CO.OK \\ | \\ CH_2 \\ | \\ CH_2.OH \end{array} + NH_3$$

Ethene-lactic acid must be regarded as the first oxidation-product of primary propene alcohol, but it has not yet been obtained from this compound. It is a monobasic acid, as well as a primary alcohol, whilst common or *ethidene-lactic acid* is a secondary alcohol.

On oxidizing the former with dilute chromic acid, it is converted into bibasic *malonic acid,* whilst common lactic acid is resolved by oxidation into acetic acid and formic acid (or carbon dioxide and water):—

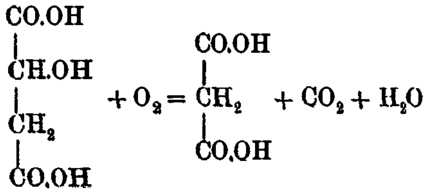
(1) 

$$\begin{array}{l}CO.OH\\ |\\ CH_2\\ |\\ CH_2.OH\end{array} + O_2 = \begin{array}{l}CO.OH\\ |\\ CH_2\\ |\\ CO.OH\end{array} + H_2O$$

(2) 

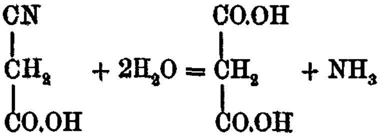
$$\begin{array}{l}CO.OH\\ |\\ CH.OH\\ |\\ CH_3\end{array} + O_2 = \begin{array}{l}CO.OH\\ |\\ CH_3\end{array} + CO_2 + H_2O$$

Malonic Acid $C_3H_4O_4$.—This acid was first obtained by the oxidation of malic acid:—



$$\begin{array}{l}CO.OH\\ |\\ CH.OH\\ |\\ CH_2\\ |\\ CO.OH\end{array} + O_2 = \begin{array}{l}CO.OH\\ |\\ CH_2\\ |\\ CO.OH\end{array} + CO_2 + H_2O$$

It is also formed by the oxidation of ethene-lactic acid and by heating cyanacetic acid with potash solution:—

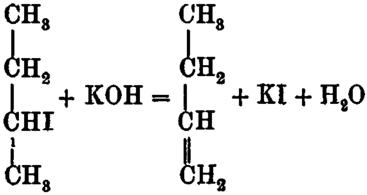


$$\begin{array}{l}CN\\ |\\ CH_2\\ |\\ CO.OH\end{array} + 2H_2O = \begin{array}{l}CO.OH\\ |\\ CH_2\\ |\\ CO.OH\end{array} + NH_3$$

Malonic acid crystallizes in large thin plates, melting at 132°. On heating it stronger, it decomposes into carbon dioxide and acetic acid. The malonates of the alkali-metals are readily soluble in water, those of the other metals sparingly soluble, or insoluble.

BUTENE COMPOUNDS.

a Butene or Butylene C_4H_8 is found in coal gas, and in large quantities in the gas obtained from fatty oils. Pure butene is readily obtained by heating secondary butyl iodide with an alcoholic solution of caustic potash:—

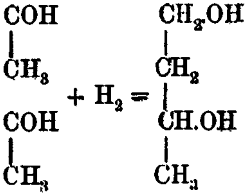


$$\begin{array}{l}CH_3\\ |\\ CH_2\\ |\\ CHI\\ |\\ CH_3\end{array} + KOH = \begin{array}{l}CH_3\\ |\\ CH_2\\ |\\ CH\\ \|\\ CH_2\end{array} + KI + H_2O$$

It is a colourless gas which by exposure to strong cold condenses to a limpid liquid, boiling at + 1°.

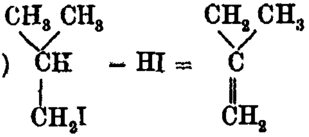
Butene Dibromide $C_4H_8Br_2$ is a heavy colourless liquid boiling at 159°. Butene combines readily with fuming hydriodic acid, secondary butyl iodide being formed. It is also slowly absorbed by an aqueous solution of hypochlorous acid, with the formation of *butene chlorhydrate* $C_4H_8\left\{\begin{array}{l}OH\\ Cl\end{array}\right.$, which, by the action of sodium amalgam and water, is converted into secondary butyl alcohol.

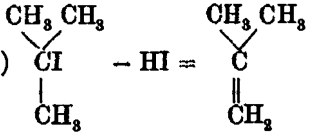
Butene Glycol $C_4H_8(OH)_2$.—This body is formed, but only in a small quantity, together with alcohol, by the action of sodium amalgam on a weak acid aqueous solution of aldehyde. It is a thick, colourless, sweet liquid, boiling at 204°. By oxidation it yields acetic acid and oxalic acid; this proves that its constitution and mode of formation is as follows:—



$$\begin{array}{l}COH\\ |\\ CH_3\\ \\ COH\\ |\\ CH_3\end{array} + H_2 = \begin{array}{l}CH_2OH\\ |\\ CH_2\\ |\\ CH.OH\\ |\\ CH_3\end{array}$$

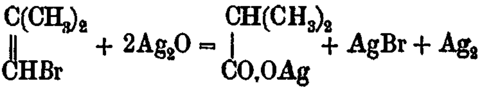
Isobutene or Dimethyl-ethene C_4H_8 has been obtained (1) by heating isobutyl alcohol with zinc chloride, (2) by passing the vapour of amyl alcohol through a red-hot tube, and (3), together with tetramethylbutane (so called dibutyl), in the electrolysis of potassium valerate. The pure hydrocarbon is most readily produced by the action of alcoholic potash solution on isobutyl iodide and tertiary butyl iodide:—

(1)


(2)


Isobutene may be condensed to a liquid, boiling at −7°, and possessing an unpleasant smell like coal gas. It is easily transformed again into isobutyl and tertiary butyl compounds (see Butyl Compounds).

Isobutene Dibromide $C_4H_8Br_2$ boils at 156° and is easily converted into *isobutene glycol* $C_4H_8(OH)_2$, a thick liquid possessing a sweet taste and boiling at 183°. When the dibromide is heated with alcoholic potash it loses hydrobromic acid and is converted into *monobromisobutene* C_4H_7Br, which by the action of silver oxide yields isobutyric acid:—



$$\begin{array}{l}C(CH_3)_2\\ \| \\ CHBr\end{array} + 2Ag_2O = \begin{array}{l}CH(CH_3)_2\\ | \\ CO.OAg\end{array} + AgBr + Ag_2$$

β Butene or Ethyl-vinyl C_4H_8 is produced by heating zinc-ethyl and monobromethene (vinyl-bromide) in sealed tubes to 140°. It boils at −5°, and forms a dibromide boiling at 166°. From its mode of formation it might have been expected that it was identical with *a* butene, but as this is not the case, and as it also differs from isobutene, it must represent the third modification of butene, of which, according to theory, three isomerides can exist (see page 176). The reaction by which it is formed may be expressed thus:—

$$CH_2{=}CH + CH_2{—}CH_3 = CH_3{—}CH{=}CH{—}CH_3$$

There exist similar reactions in which, by joining two radicals together, the double linking of two carbon-atoms is shifted in the same way (see Crotonitrile).

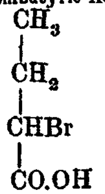
OXYBUTYRIC ACIDS $C_4H_8O_3$.

Butylactic Acid or a Oxybutyric Acid.—When butyric acid is heated with bromine, *a bromobutyric acid* is formed, a liquid boiling with partial decomposition at about 217°. On heating it with water and silver oxide it yields *a oxybutyric acid* $C_3H_6(OH)CO_2H$, forming deliquescent crystals grouped in rosettes. The *α* oxybutyrates crystallize well; the zinc-salt is sparingly soluble in water.

By the action of ammonia upon *α* bromobutyric acid, *butalanine* or *α amidobutyric acid* $C_3H_6(NH_2)CO_2H$ is obtained, which crystallizes in small needles.

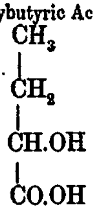
The formation of oxybutyric acid from butyric acid corresponds to that of lactic acid from propionic acid, from which it follows that both oxyacids must have a similar constitution, *i.e.* the hydroxyl being combined with that carbon atom which is linked to the carboxyl. This appears the more probable as it has been found as a rule that by the action of chlorine or bromine upon carbon atoms substitution always takes place in the neighbourhood of other negative elements (Cl, Br, O). The constitution of *α* oxybutyric acid is explained by the following formulæ :—

α Brombutyric Acid.



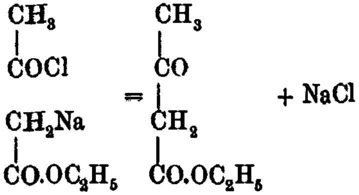
$$\begin{array}{l} \mathrm{CH_3} \\ | \\ \mathrm{CH_2} \\ | \\ \mathrm{CHBr} \\ | \\ \mathrm{CO.OH} \end{array}$$

β Oxybutyric Acid.



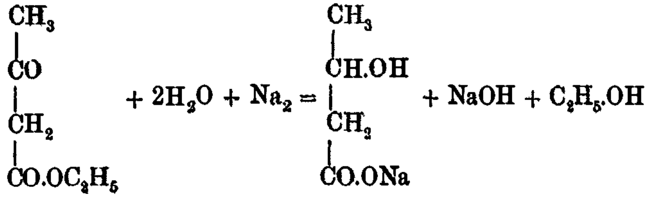
$$\begin{array}{l} \mathrm{CH_3} \\ | \\ \mathrm{CH_2} \\ | \\ \mathrm{CH.OH} \\ | \\ \mathrm{CO.OH} \end{array}$$

β Oxybutyric Acid.—By acting with acetyl chloride on monosodacetic ether, the ethyl ether of acetyl-acetic acid is formed :—



$$\begin{array}{l} \mathrm{CH_3} \\ | \\ \mathrm{COCl} \\ \\ \mathrm{CH_2Na} \\ | \\ \mathrm{CO.OC_2H_5} \end{array} = \begin{array}{l} \mathrm{CH_3} \\ | \\ \mathrm{CO} \\ | \\ \mathrm{CH_2} \\ | \\ \mathrm{CO.OC_2H_5} \end{array} + \mathrm{NaCl}$$

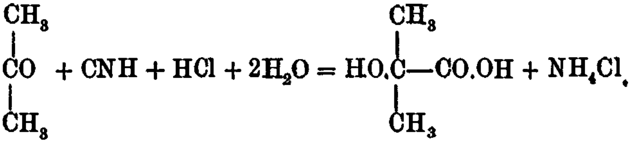
On treating this ether with water and sodium amalgam it is converted into sodium *β* oxybutyrate :—



$$\begin{array}{l} \mathrm{CH_3} \\ | \\ \mathrm{CO} \\ | \\ \mathrm{CH_2} \\ | \\ \mathrm{CO.OC_2H_5} \end{array} + 2\mathrm{H_2O} + \mathrm{Na_2} = \begin{array}{l} \mathrm{CH_3} \\ | \\ \mathrm{CH.OH} \\ | \\ \mathrm{CH_2} \\ | \\ \mathrm{CO.ONa} \end{array} + \mathrm{NaOH} + \mathrm{C_2H_5.OH}$$

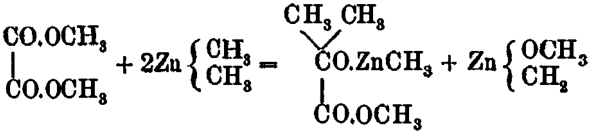
By decomposing this salt with sulphuric acid, *β* oxybutyric acid is obtained as a thick, syrupy, and very deliquescent liquid. The *β* oxybutyrates are very soluble in water, the zinc salt forming a brittle, amorphous, and deliquescent mass.

Oxy-isobutyric Acid is produced by oxidizing isobutene glycol, and by the action of caustic baryta on bromisobutyric acid. The same acid has been produced synthetically from acetone, by a reaction quite analogous to that by which lactic acid is obtained from aldehyde. When a mixture of prussic acid, acetone, and hydrochloric acid, after standing for some weeks, is boiled, the following reaction takes place:—



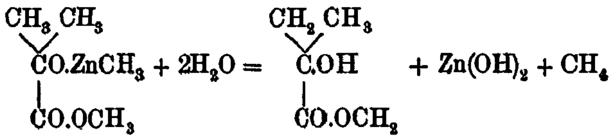
$$\begin{array}{c}\mathrm{CH_3}\\ | \\ \mathrm{CO}\\ | \\ \mathrm{CH_3}\end{array} + \mathrm{CNH} + \mathrm{HCl} + 2\mathrm{H_2O} = \mathrm{HO.}\begin{array}{c}\mathrm{CH_3}\\ | \\ \mathrm{C}\\ | \\ \mathrm{CH_3}\end{array}\!\!-\mathrm{CO.OH} + \mathrm{NH_4Cl}.$$

By this reaction the acid was first obtained, and was therefore called *acetonic acid*. Another synthetical process for preparing it consists in heating methyl oxalate with methyl iodide and zinc, zinc-methyl being first formed, which acts on the methyl ether in the following way:—



$$\begin{array}{l}\mathrm{CO.OCH_3}\\ | \\ \mathrm{CO.OCH_3}\end{array} + 2\mathrm{Zn}\left\{\begin{array}{l}\mathrm{CH_3}\\ \mathrm{CH_3}\end{array}\right. = \begin{array}{l}\mathrm{CH_3\ CH_3}\\ \quad\diagdown\!\diagup \\ \quad\mathrm{CO.ZnCH_3}\\ \quad | \\ \quad\mathrm{CO.OCH_3}\end{array} + \mathrm{Zn}\left\{\begin{array}{l}\mathrm{OCH_3}\\ \mathrm{CH_2}\end{array}\right.$$

On adding water to the resulting crystalline mass, marsh-gas is given off, and the methyl-ether of oxy-isobutyric acid (dimethyl-oxalic acid) is formed:—



$$\begin{array}{l}\mathrm{CH_3\ CH_3}\\ \quad\diagdown\!\diagup \\ \quad\mathrm{CO.ZnCH_3}\\ \quad | \\ \quad\mathrm{CO.OCH_3}\end{array} + 2\mathrm{H_2O} = \begin{array}{l}\mathrm{CH_2\ CH_3}\\ \quad\diagdown\!\diagup \\ \quad\mathrm{C.OH}\\ \quad | \\ \quad\mathrm{CO.OCH_2}\end{array} + \mathrm{Zn(OH)_2} + \mathrm{CH_4}$$

Oxy-isobutyric acid is readily soluble in water, and crystallizes in long needles, melting at 79°, boiling at 212°, but readily subliming at a lower temperature. The zinc-salt is sparingly soluble in water, and crystallizes in small hexagonal plates.

SUCCINYL COMPOUNDS.

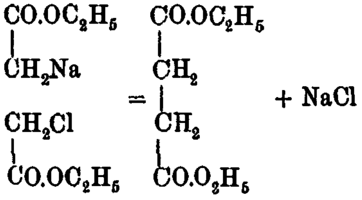
SUCCINIC ACID $C_4H_6O_4$.

This acid occurs in amber and some other resins, and in several plants (*Artemisia Absinthium, Lactuca virosa*), and has also been found in small quantities in the animal organism. Succinic acid is frequently met with amongst the products formed by the action of nitric acid upon many carbon compounds. Thus all fatty acids containing more than four atoms of carbon, when boiled with nitric acid yield succinic acid and other acids of the same series.

Succinic acid is also produced by different kinds of fermentation, in small quantities in vinous fermentation, in larger quantities in the fermentation of malic acid, which acid, as well as tartaric acid, is also readily converted into succinic acid by reduction (*vide* these acids).

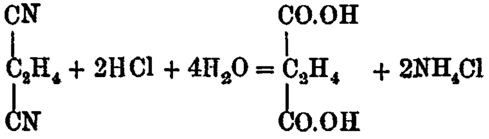
Succinic acid has also been obtained artificially from acetic acid, ethene, and β chloropropionic acid:—

(1) When sodacetic ether is heated with ethyl chloracetate, ethyl succinate is formed:—



$$\begin{array}{l} CO.OC_2H_5 \\ | \\ CH_2Na \\ \\ CH_2Cl \\ | \\ CO.OC_2H_5 \end{array} = \begin{array}{l} CO.OC_2H_5 \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CO.O_2H_5 \end{array} + NaCl$$

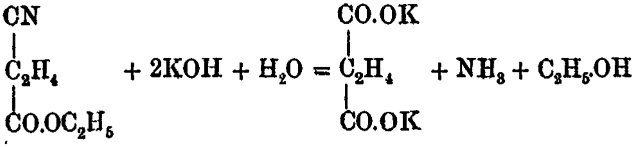
(2) *Succinonitrile* $C_2H_4(CN)_2$ is produced by heating ethene dibromide with potassium cyanide and alcohol; it is a crystalline solid, melting at 37° to a brown, oily liquid, and decomposing at a higher temperature. On boiling it with caustic potash or with hydrochloric acid or nitric acid, it yields succinic acid:—



$$\begin{array}{l} CN \\ | \\ C_2H_4 \\ | \\ CN \end{array} + 2HCl + 4H_2O = \begin{array}{l} CO.OH \\ | \\ C_2H_4 \\ | \\ CO.OH \end{array} + 2NH_4Cl$$

Succinonitrile has also been obtained by the electrolysis of potassium cyanacetate, a reaction which is quite analogous to the formation of ethane (dimethyl) from potassium acetate.

(3) When the ethyl-ether of *β chloropropionic acid* (see Glyceric Acid) is heated with potassium cyanide, the ethyl-ether of β cyanopropionic acid is formed. This ether, when heated with caustic potash, yields potassium succinate and alcohol:—



$$\begin{array}{l} CN \\ | \\ C_2H_4 \\ | \\ CO.OC_2H_5 \end{array} + 2KOH + H_2O = \begin{array}{l} CO.OK \\ | \\ C_2H_4 \\ | \\ CO.OK \end{array} + NH_3 + C_2H_5.OH$$

To obtain succinic acid in quantity, amber is subjected to destructive distillation, and the aqueous portion of the distillate heated to the boiling-point and filtered. On cooling, crude succinic acid crystallizes out, which is easily freed from adhering empyreumatic oils by heating it with nitric acid.

It may also conveniently be prepared from the crude calcium salt of malic acid, which can be procured in large quantities from the unripe berries of the mountain ash or from rhubarb-stalks (see Malic Acid). On adding six parts of water and a fourth part of brewer's yeast to this salt, and keeping the mixture at a temperature of 30°—40° for a few days, carbon dioxide is evolved and acetic acid and calcium succinate are formed, probably according to the following two reactions:—

$$(1)\quad C_4H_6O_5 + H_2O = C_2H_4O_2 + 2CO_2 + H_2$$

$$(2)\quad C_4H_6O_5 + H_2 = C_4H_6O_4 + H_2O$$

To obtain the free acid, the calcium salt is decomposed by sulphuric acid.

Succinic acid crystallizes in monoclinic prisms, melting at 180° and decomposing at 235° into water and succinic anhydride. It is soluble in about twenty-three parts of cold water and very readily in boiling water. By passing a galvanic current through a concentrated solution of potassium succinate the acid is decomposed into ethene, carbon dioxide, and hydrogen:—

$$C_2H_4\left\{\begin{matrix} CO_2H \\ CO_2H \end{matrix}\right. = C_2H_4 + 2CO_2 + H_2$$

When an aqueous solution of the acid containing an uranic salt is exposed to sunlight it splits up into propionic acid and carbon dioxide:—

$$C_2H_4\left\{\begin{matrix} CO_2H \\ CO_2H \end{matrix}\right. = CO_2 + C_2H_5.CO_2H$$

The succinates of the alkali-metals are readily soluble in water; those of the other metals either sparingly soluble or insoluble. By adding a neutral solution of ferric chloride to a neutral succinate a brown gelatinous precipitate of ferric succinate is formed. This reaction is made use of for the detection of this acid and for the separation of iron from manganese.

Ethyl Succinate $C_4H_4O_4\left\{\begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix}\right.$ is a colourless, oily liquid, insoluble in water, and boiling at 217°. It is obtained by passing hydrochloric acid gas into a solution of succinic acid in alcohol.

Ethylsuccinic Acid $C_4H_4O_4\left\{\begin{matrix} C_2H_5 \\ H \end{matrix}\right.$ is produced by heating succinic anhydride with absolute alcohol. It is a syrupy, sour liquid, soluble in water and forming soluble salts.

Succinic Anhydride $C_4H_4O_3$ is most conveniently prepared by distilling succinic acid with phosphorus pentoxide. It forms shining crystals, melting at 120° and boiling at 250°. On boiling it with water succinic acid is again formed:—

$$C_2H_4\left\{\begin{matrix}CO\\CO\end{matrix}\right\rangle O + H_2O = C_2H_4\left\{\begin{matrix}CO.OH\\CO.OH\end{matrix}\right.$$

Succinyl Chloride $C_2H_4\left\{\begin{matrix}COCl\\COCl\end{matrix}\right.$ is produced by the action of phosphorus pentachloride upon the acid or the anhydride. It is an oily liquid, boiling at 190° and solidifying at 0° to tabular crystals. It has a suffocating smell, fumes in the air, and forms, in contact with water, succinic acid and hydrochloric acid, and with alcohol it yields ethyl succinate and hydrochloric acid.

Sulphosuccinic Acid $C_2H_3\left\{\begin{matrix}CO.OH\\SO_2.OH\\CO.OH\end{matrix}\right.$.—This strong tribasic acid is formed by the action of sulphur trioxide upon succinic acid, and forms deliquescent crystals.

AMIDES OF SUCCINIC ACID.

Succinamide $C_2H_4\left\{\begin{matrix}CO.NH_2\\CO.NH_2\end{matrix}\right.$.—When ammonia is added to ethyl succinate the amide separates out in fine white needles, which are readily soluble in hot but sparingly in cold water, and insoluble in spirits of wine. On heating it melts, and at 200° decomposes into ammonia and *succinimide* $C_2H_4\left\{\begin{matrix}CO\\CO\end{matrix}\right\}NH$, a compound which is also produced by the action of ammonia upon succinic anhydride, and by the rapid distillation of ammonium succinate. Succinimide is readily soluble in water and alcohol, crystallizing in rhombic tables containing one molecule of water, which is readily given off on exposure to the air. The anhydrous compound melts at 126° and boils at 288°. On heating it with alcoholic ammonia to 100° it is reconverted into succinamide. By adding an ammoniacal solution of silver nitrate to an alcoholic solution of succinimide, *silver-succinimide* $C_2H_4(CO)_2NAg$ is formed, which crystallizes in four-sided prisms. On boiling it with aqueous ammonia it takes up water, and is converted into *silver succinamate* $C_2H_4\left\{\begin{matrix}CO.NH_2\\CO.OAg\end{matrix}\right.$. The free succinamic acid forms colourless crystals which sublime on heating; it is soluble in water, and combines with it to form acid ammonium succinate.

SUBSTITUTION-PRODUCTS OF SUCCINIC ACID.

When succinic acid is heated with bromine and water in sealed tubes, two substituted acids are simultaneously produced.

Monobromosuccinic Acid forms colourless crystals readily soluble in water. On boiling its solution with silver oxide, malic acid is formed:—

$$C_2H_3Br\left\{\begin{matrix}CO.OH\\CO.OH\end{matrix}\right. + AgOH = C_2H_3(OH)\left\{\begin{matrix}CO.OH\\CO.OH\end{matrix}\right. + AgBr$$

Bibromosuccinic Acid is sparingly soluble in cold water and crystallizes from a hot solution in prisms. It is also formed by heating succinyl chloride with bromine and decomposing the bibromosuccinic chloride thus formed with water. When sodium bibromosuccinate is boiled with water it yields *acid sodium monobromomalate*:—

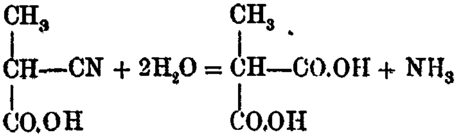
$$C_2H_2Br_2\left\{\begin{matrix}CO.ONa\\CO.ONa\end{matrix}\right. + H_2O = C_2H_2(OH)Br\left\{\begin{matrix}CO.OH\\CO.ONa\end{matrix}\right. + NaBr$$

By boiling the free acid with silver oxide and water it is converted into tartaric acid:—

$$C_2H_2Br_2\left\{\begin{matrix}CO.OH\\CO.OH\end{matrix}\right. + Ag_2O + H_2O = C_2H_2(OH)_2\left\{\begin{matrix}CO.OH\\CO.OH\end{matrix}\right. + 2AgBr$$

ISOSUCCINIC ACID.

This isomeride of succinic acid has been obtained from *a* bromopropionic acid (*see* Lactic Acid) by a reaction analogous to that by which *β* bromopropionic acid has been transformed into succinic acid. By heating *a* bromopropionic acid with potassium cyanide it is converted into *a cyanopropionic acid*, which, when boiled with potash solution, yields isosuccinic or *methyl-malonic acid*:—



$$\begin{array}{l}CH_3\\|\\CH—CN\\|\\CO.OH\end{array} + 2H_2O = \begin{array}{l}CH_3\\|\\CH—CO.OH\\|\\CO.OH\end{array} + NH_3$$

It forms colourless crystals, being more freely soluble in water than succinic acid; the solution of a neutral isosuccinate is not precipitated by ferric chloride. It melts at 129°·5 and decomposes when heated above this temperature into carbon dioxide and propionic acid. This acid is therefore a much less stable compound than succinic acid, the cause of this being that it contains two carboxyls combined with the same carbon atom. In the chapter on the constitution of the carbon compounds it has already been pointed out that in carbon compounds containing oxygen the carbon group is much more readily decomposed than in compounds containing no oxygen. and the two succinic acids show that such a separation of carbon atoms takes place more readily, the nearer together the oxygen atoms are grouped in the molecule.

MALIC ACID $C_4H_6O_5$

Malic acid and tartaric acid, two compounds which are very widely distributed in the vegetable kingdom, are very nearly related to succinic acid, bearing similar relations to the latter as glycollic acid does to acetic acid; and therefore, although they have to be regarded as compounde of triad and tetrad-radicals, they will most conveniently be treated here.

Malic Acid is found in most kinds of sour fruit, chiefly in unripe apples, and in the berries of the mountain ash, and also in currants, sour cherries, in the stalks and leaves of rhubarb, &c. Sweet cherries contain neutral potassium malate.

The acid is readily obtained from rhubarb-stalks or from the berries of the mountain ash at the time when they begin to ripen. The stalks or berries are ground to a pulp and pressed out. The juice is boiled and nearly neutralized with milk of lime. On boiling the filtered liquid for some time calcium malate separates out as a granular powder, which is washed with cold water and dissolved in hot dilute nitric acid. On cooling, acid calcium malate is obtained in large crystals, which are separated from the mother-liquid, and dissolved in water. On adding lead acetate to this solution lead malate is precipitated, which is washed and then decomposed by hydrogen sulphide. Malic acid is obtained on evaporating the aqueous solution in groups of small colourless and deliquescent prisms, having a strong and agreeable sour taste. Its solution turns the plane of polarized light to the left; whilst the acid obtained artificially from succinic acid is optically inactive.

On heating malic acid with concentrated hydriodic acid, it is reduced to succinic acid:—

$$C_2H_3(OH)(CO_2H)_2 + 2HI = C_2H_4(CO_2H)_2 + H_2O + I_2$$

When malic acid is heated with hydrobromic acid it is converted into monobromosuccinic acid:—

$$C_2H_3(OH)(CO_2H)_2 + HBr = C_2H_3Br(CO_2H)_2 + H_2O$$

The malates of the alkali-metals are readily soluble in water.

Normal Calcium Malate $C_4H_4O_5Ca + 2H_2O$ crystallizes in large plates; on boiling its aqueous solution for some time it separates as a granular powder $C_4H_4O_5Ca + H_2O$. *Acid calcium malate*

$(C_4H_5O_5)_2Ca + 8H_2O$ forms large transparent crystals. *Lead malate* is a curdy precipitate which after some time changes into a crystalline mass. On heating it with water a small portion dissolves, whilst the remainder melts.

Malic acid contains one alcoholic hydroxyl, and forms consequently ethers with acid radicals and with alcohol radicals.

On passing hydrochloric acid gas into a solution of malic acid in alcohol, *ethyl malate* $C_2H_3(OH)\left\{\begin{array}{l}CO.OC_2H_5\\CO.OC_2H_5\end{array}\right.$, a neutral liquid, which decomposes on heating, is formed, together with the monobasic *ethylmalic acid* $C_2H_3(OH)\left\{\begin{array}{l}CO.OH\\CO.OC_2H_5\end{array}\right.$.

By the action of acetyl chloride upon ethyl malate the ethyl-ether of *acetylmalic acid* is formed. This acid has the following constitution:—

$$\begin{array}{l}CO.OH\\|\\CH.OC_2H_3O\\|\\CH_2\\|\\CO.OH\end{array}$$

Ethyl acetylmalate is a liquid, boiling at 258°; on heating it with caustic potash it is resolved into potassium malate, potassium acetate, and ethyl alcohol.

AMIDES OF MALIC ACID.

Malamide $C_2H_3(OH)\left\{\begin{array}{l}CO.NH_2\\CO.NH_2\end{array}\right.$ is produced by the action of ammonia upon an alcoholic solution of ethyl malate. It forms colourless crystals, and combines readily with water, yielding ammonium malate.

Asparagin or Amidosuccinamic Acid $CH_3(NH_2)\left\{\begin{array}{l}CO.NH_2\\CO.OH\end{array}\right.$ is found in asparagus-shoots, in the roots of the marsh mallow and of liquorice, in potatoes, and in large quantities in young vetches, peas, and beans. To prepare it, young vetches before they get into flower are pressed out, the juice heated to the boiling-point, filtered, and evaporated to the consistency of a syrup. On standing for some time, asparagin crystallizes out. It forms large transparent crystals containing two molecules of water. It is a weak monobasic acid, forming crystalline salts; at the same time it is an amine and combines with acids.

Nitrous acid decomposes it with the formation of malic acid.

Aspartic Acid or Amidosuccinic Acid $C_2H_3(NH_2)\left\{\begin{array}{l}CO.OH\\CO.OH\end{array}\right.$.— The ammonium salt of this acid is produced by heating an aqueous solution of asparagin to 120°. To prepare the acid, asparagin is boiled with baryta-water; ammonia is given off, and barium aspartate is formed, which is decomposed by sulphuric acid, and the solution evaporated to crystallization. It is a bibasic acid, forming crystalline salts. When the acid silver salt is heated with ethyl iodide the ether $C_2H_3(NH_2)\begin{cases}CO.OH\\CO.OC_2H_5\end{cases}$ is formed, a crystalline solid, which by the action of aqueous ammonia yields asparagin and ethyl alcohol.

FUMARIC ACID AND MALEIC ACID $C_4H_4O_4$.

These two isomeric acids are obtained by heating malic acid :—

$$C_4H_6O_5 = C_4H_4O_4 + H_2O$$

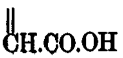
Maleic acid distils over together with water, and is obtained in crystals on evaporating the distillate. It forms large plates, and is very soluble in water. It melts at about 130°, and when kept at that temperature for some time it is transformed into fumaric acid, which on stronger heating is decomposed into water and maleic anhydride $C_4H_2O_3$, a compound which again combines with water, forming maleic acid.

Fumaric Acid occurs also in many plants (Corydalis, Fumaria, and Glaucium species).

It is most conveniently obtained by exposing malic acid for some time to a temperature of 120°—150°. It crystallizes in prisms and is sparingly soluble in water.

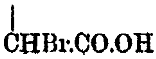
The two isomeric acids combine with nascent hydrogen, both being converted into succinic acid. They also combine readily with bromine; fumaric acid yielding bibromosuccinic acid, from which it follows that the constitution of fumaric acid is expressed by the following formula:—

Fumaric Acid.



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

Bibromosuccinic Acid.



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

Maleic acid forms with bromine *isobibromosuccinic acid*, the constitution of which appears to be $\begin{array}{l}CH_2.CO.OH\\ |\\ CBr_2.CO.OH\end{array}$, according to which maleic acid would contain an atom of carbon with free combining units.

TARTARIC ACID $C_4H_6O_6$.

This acid exists in different isomeric modifications which differ from each other by their optical properties.

(1) *Dextrotartaric Acid or Ordinary Tartaric Acid* occurs in the free state, and as an acid potassium salt in many kinds of fruit, chiefly in pine-apples, tamarinds, and in grapes. It is also formed by oxidizing milk-sugar with nitric acid. It is prepared on the large scale from *crude tartar* or impure acid potassium tartrate, which is deposited in wine casks, the salt being less soluble in dilute alcohol than in water. Tartar is purified by dissolving it in hot water, decolorizing the solution with animal charcoal, and subsequent crystallization. The *cream of tartar* thus obtained is boiled with water and chalk, insoluble calcium tartrate is formed, whilst the solution contains normal potassium tartrate, which is also converted into the calcium salt by precipitation with calcium chloride. The washed calcium tartrate is decomposed with dilute sulphuric acid, and the solution evaporated to crystallization.

Tartaric acid crystallizes in large transparent monoclinic prisms possessing a very sour taste; it is readily soluble in water, and its aqueous solution turns the plane of polarized light to the right.

When it is heated to 180° it melts, and is converted into isomeric *metatartaric acid*, an amorphous deliquescent mass, which after some time becomes crystalline. The metatartrates are very readily soluble in water, and are reconverted into ordinary tartrates on boiling their solutions.

On heating tartaric acid for some time water is given off and *ditartaric acid* $C_8H_{10}O_{11}$ is formed, a compound having probably a constitution similar to that of the so-called lactic anhydride. It is amorphous and forms uncrystallizable salts, which on boiling their aqueous solution take up water and are converted first into metatartrates and then into ordinary tartrates.

When tartaric acid is rapidly heated it swells up, and is converted into *tartaric anhydride* or *tartrelic acid* $C_4H_4O_5$, a yellow deliquescent mass, which also combines again with water to tartaric acid.

When tartaric acid is heated with concentrated hydriodic acid and phosphorus, it is reduced first to malic acid and then to succinic acid.

TARTRATES.

Normal Potassium Tartrate $C_4H_4O_6\left\{\begin{matrix}K\\K\end{matrix}\right.$ crystallizes in monoclinic prisms, and is readily soluble in water. On adding an acid to its solution the acid salt or *cream of tartar* $C_4H_4O_6\left\{\begin{matrix}K\\H\end{matrix}\right.$ is precipitated as a crystalline powder, which dissolves in about 240 parts of cold water, but more freely in boiling water. The two sodium tartrates are both readily soluble.

Potassium Sodium Tartrate or Rochelle Salt $C_4H_4O_6\left\{\begin{matrix}K\\Na\end{matrix}\right. + 4H_2O$ is obtained by neutralizing a boiling solution of sodium carbonate with cream of tartar. It forms large rhombic prisms, and is freely soluble in water.

Calcium Tartrate $C_4H_4O_6Ca + 4H_2O$ occurs in crude tartar; it is a crystalline powder, insoluble in water, but soluble in weak acids, in ammonium salts, and alkalis.

Tartar Emetic $C_4H_4O_6\left\{\begin{matrix}K\\SbO\end{matrix}\right.$ is obtained by boiling cream of tartar with water and antimony trioxide. It crystallizes in shining rhombic octahedrons, containing half a molecule of water, and dissolving in fourteen parts of cold and two parts of boiling water.

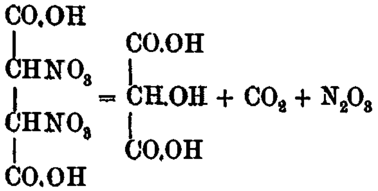
A similarly constituted compound, called *tartarus boratus* $C_4H_4O_6\left\{\begin{matrix}K\\BoO\end{matrix}\right.$, is obtained as an amorphous, deliquescent, and very sour mass on evaporating a solution of boric acid with cream of tartar.

ETHERS OF TARTARIC ACID.

Ethyl Tartrate $C_4H_4O_6\left\{\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right.$ is a non-volatile liquid, which is formed by passing hydrochloric acid into an alcoholic solution of tartaric acid. On evaporating a solution of tartaric acid in absolute alcohol, *ethyl-tartaric acid* $C_4H_4O_6\left\{\begin{matrix}H\\C_2H_5\end{matrix}\right.$ is left behind as a crystalline deliquescent mass. By the action of acetyl chloride on ethyl tartrate the ethyl ethers of *acetyltartaric acid* and *diacetyltartaric acid* are formed. These acids have the following constitution:—

Tartaric Acid.	Acetyltartaric Acid.	Diacetyltartaric Acid.
$C_2H_2\left\{\begin{matrix}CO.OH\\OH\\OH\\CO.OH\end{matrix}\right.$	$C_2H_2\left\{\begin{matrix}CO.OH\\OC_2H_3O\\OH\\CO.OH\end{matrix}\right.$	$C_2H_2\left\{\begin{matrix}CO.OH\\OC_2H_3O\\OC_2H_3O\\CO.OH\end{matrix}\right.$

Nitrotartaric Acid $C_4H_2(NO_3)_2O_4$.—This compound is obtained by dissolving tartaric acid in concentrated nitric acid and adding sulphuric acid to the solution. A gelatinous mass separates out, which is dried on porous porcelain plates, and dissolved in tepid water. On cooling the solution to 0°, nitrotartaric acid crystallizes out. This compound is a nitric ether, the two alcoholic hydroxyls of tartaric acid being replaced by NO_3. It is a very unstable body; its aqueous solution decomposes on spontaneous evaporation, and leaves *tartronic acid* or *oxymalonic acid* $C_3H_4O_5$ behind:—



$$\begin{array}{l} CO.OH \\ | \\ CHNO_3 \\ | \\ CHNO_3 \\ | \\ CO.OH \end{array} = \begin{array}{l} CO.OH \\ | \\ CH.OH \\ | \\ CO.OH \end{array} + CO_2 + N_2O_3$$

On heating an aqueous solution of nitrotartaric acid it is oxidized to oxalic acid. Ammonium sulphide acts on it as on other nitric ethers, tartaric acid being formed again.

RACEMIC ACID AND LEVOTARTARIC ACID.

Racemic acid occurs together with tartaric acid in several kinds of tartar. It crystallizes in transparent rhombic prisms $C_4H_6O_6 + H_2O$, and is rather less soluble than tartaric acid; but in all other respects a very great resemblance exists between these two acids and their salts, the chief difference being that calcium racemate is insoluble in ammonium salts, and further, that crystallized normal racemates, containing one metal, do not exhibit hemihedral faces, like the crystals of the corresponding tartrates.

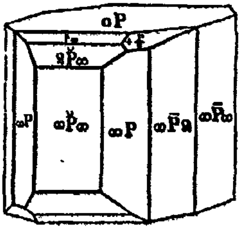


FIG. 10.

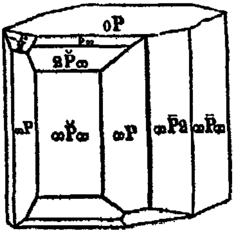
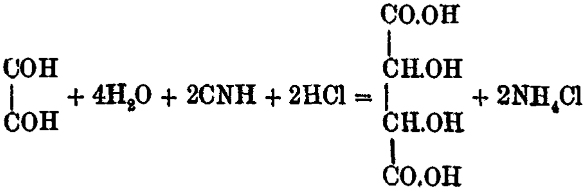


FIG. 11.

By neutralizing acid sodium racemate with ammonia, and allowing the solution to crystallize slowly, two varieties of crystals are obtained, each of them containing hemihedral faces ($\frac{f}{2}$) (see Figs. 10 and 11), equal in number, and exactly similar in form, but developed on opposite sides of the two crystals, so that each of them may be regarded as a reflected image of the other. On carefully separating these crystals and converting them into the acids, two acids are obtained, one being common or dextrotartaric acid, and the other a very similar acid called *levotartaric acid*, because it possesses left-handed polarization. On dissolving equal parts of the two acids in water, and allowing them to crystallize, we obtain again optically inactive racemic acid, which therefore is a combination of the two active acids.

INACTIVE TARTARIC ACID.

This acid, which cannot be decomposed into the two active modifications, has been produced artificially from bibromosuccinic acid (see page 222). An acid which is probably identical with this inactive acid is formed by boiling oxalaldehyde (glyoxal) with prussic acid and hydrochloric acid, a synthetical process quite analogous to the formation of lactic acid from aldehyde:—



$$\begin{array}{l}COH\\|\\COH\end{array} + 4H_2O + 2CNH + 2HCl = \begin{array}{l}CO.OH\\|\\CH.OH\\|\\CH.OH\\|\\CO.OH\end{array} + 2NH_4Cl$$

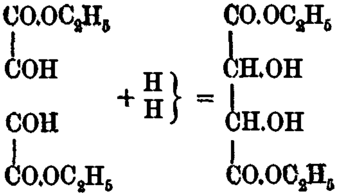
It has already been mentioned that by acting with sodium amalgam on an alcoholic solution of ethyl oxalate, glycollic and tartaric acids are formed, the latter being no doubt identical with that from glyoxal. The reactions by which these acids are produced can be easily explained.

The sodium forms with the alcohol, sodium ethylate, and the nascent hydrogen converts a part of the oxalic ether first into ethyl glyoxylate and then into the glycollate:—

$$(1)\quad \left\{\begin{array}{l}CO(OC_2H_5)\\CO(OC_2H_5)\end{array}\right. + H_2 = \left\{\begin{array}{l}COH\\CO(OC_2H_5)\end{array}\right. + HO.C_2H_5$$

$$(2)\quad \left\{\begin{array}{l}COH\\CO(OC_2H_5)\end{array}\right. + H_2 = \left\{\begin{array}{l}CH_2.OH\\CO(OC_2H_5)\end{array}\right.$$

But the two atoms of hydrogen can enter the glyoxylate one after the other; if only one enters we have an unsaturated molecule, of which two can combine and form ethyl tartrate:—



$$\begin{array}{l}CO.OC_2H_5\\|\\COH\\ \\COH\\|\\CO.OC_2H_5\end{array} + \left.\begin{array}{l}H\\H\end{array}\right\} = \begin{array}{l}CO.OC_2H_5\\|\\CH.OH\\|\\CH.OH\\|\\CO.OC_2H_5\end{array}$$

If we remember that, by simple reactions, oxalates can be formed from carbon dioxide, we see that a few steps lead us from an inorganic substance of very simple constitution to a complex organic acid. This is a point of great interest, because glycollates and tartrates occur together in grapes and the leaves of the wild vine.

The salts of inactive tartaric acid have a great resemblance to the racemates.

The different modifications of tartaric acid can be transformed into each other. Thus by combining either of the two active acids with cinchonine and heating the salts to 170°, a resinous mass is formed containing a large quantity of cinchonine racemate, and this salt when heated for a long time is converted into the salt of the inactive acid. When dextrotartaric acid is heated with a little water in sealed tubes to 165°, a small quantity of racemic acid is formed, together with a large quantity of the inactive acid, whilst when the temperature is raised to 175° chiefly racemic acid is formed. By means of this reaction inactive acid obtained synthetically from ethene has been transformed into racemic acid, which is identical with that contained in grapes, and could be resolved into the two active modifications. This is the first example of the complete synthesis of a body turning the plane of polarization.[1]

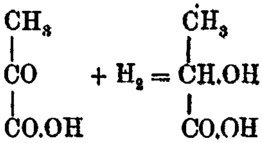
When any of the four modifications of tartaric acid is subjected to destructive distillation it gives off water and carbon dioxide, and three new acids are formed:—

$$C_4H_2O_6 = \overset{\text{Pyroracemic Acid.}}{C_3H_4O_3} + CO_2 + H_2O$$

$$2C_4H_6O_6 = \overset{\text{Pyrotartaric Acid.}}{C_5H_8O_4} + 3CO_2 + 2H_2O$$

$$3C_4H_6O_6 = \overset{\text{Pyrotritaric Acid.}}{C_7H_8O_3} + 5CO_2 + 5H_2O$$

Pyroracemic or Pyruvic Acid $C_3H_4O_3$ is a colourless liquid possessing a pungent smell like acetic acid, and boiling at 165°. It combines with nascent hydrogen, and is transformed into lactic acid, to which it stands in the same relation as dimethyl ketone to secondary propyl alcohol:—



$$\begin{array}{l} CH_3 \\ | \\ CO \\ | \\ CO.OH \end{array} + H_2 = \begin{array}{l} CH_3 \\ | \\ CH.OH \\ | \\ CO.OH \end{array}$$

On boiling pyruvic acid or a pyruvate with water it changes into a non-volatile syrupy modification, which forms amorphous salts. On heating this substance, which is probably a polymeride of the volatile acid, it is resolved into carbon dioxide and pyrotartaric acid:—

---

[1] On page 43 it is said "that no carbon compound prepared by synthesis has been found to be optically active," the above reaction not being known at the time when this was printed.

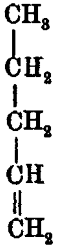
$$2C_3H_4O_3 = CO_2 + C_5H_8O_4$$

Pyrotartaric acid is homologous with oxalic acid, and will be described later on.

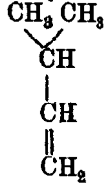
COMPOUNDS CONTAINING FIVE ATOMS OF CARBON.

Three isomeric olefines having the formula C_5H_{10} are known, viz. *pentene* or *isoamylene*, *amylene* or *amene*, and *methyl-ethylethene*:—

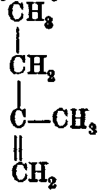
Pentene.



Amylene.



Methyl-ethylethene.



Pentene has been obtained synthetically by the action of zinc-ethyl upon allyl iodide $CH_2{=}CH{-}CH_2I$. It is also formed by heating secondary pentyl chloride with an alcoholic solution of caustic potash. It is a limpid liquid boiling at 39°. The derivatives of this hydrocarbon have been very little studied; with bromine it forms *pentene dibromide* $C_5H_{10}Br_2$, boiling between 170° and 180°.

Amylene or Isopropylethene is conveniently prepared by mixing one part of amyl alcohol with 1½ parts of fused zinc chloride, and distilling the mixture after standing for some time. The distillate contains besides amylene also polymerides as *diamylene* $C_{10}H_{20}$, *triamylene* $C_{15}H_{30}$, *tetra-amylene* $C_{20}H_{40}$, and other hydrocarbons. Amylene boils at 35°.

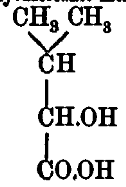
Amylene Dibromide $C_5H_{10}Br_2$ is a heavy colourless liquid boiling between 170° and 175°. On heating it with silver acetate it yields amylene diacetate, which on distillation with caustic baryta is converted into *amylene glycol* $C_5H_{10}(OH)_2$, a compound which has also been obtained by the direct union of amylene with hydrogen dioxide. It is a thick colourless liquid having a sweet taste, and boiling at 177°.

Methyl-ethylethene has been produced by the action of alcoholic potash on *dimethyl-ethylcarbyl iodide* $C(CH_3)_2(C_2H_5)I$. It is a limpid liquid having a peculiar smell, and boiling at 35°. It combines readily with fuming hydriodic acid, the tertiary iodide being re-formed.

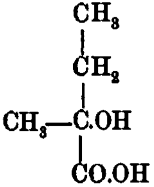
Oxyvalerianic Acid $C_5H_9(OH)O_2$ is obtained by heating bromovalerianic acid with water and silver oxide; it forms large tabular crystals melting at 80° and readily subliming. On heating bromovalerianic acid with ammonia it is converted into *amidovalerianic acid* or *butalanine* $C_5H_9(NH_2)O_2$, a compound which occurs in the spleen and the pancreas of the ox. It crystallizes in small plates, and can be sublimed.

Ethomethoxalic Acid $C_5H_9(OH)O_2$ has been obtained by heating ethyl oxalate with zinc and a mixture of ethyl- and methyl iodides. It forms colourless crystals melting at 63°. The following formulæ explain the constitution of these two isomerides:—

Oxyvalerianic Acid.



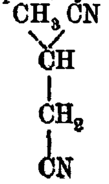
Ethomethoxalic Acid.



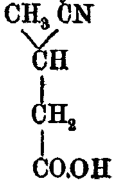
Pyrotartaric Acid or Methyl-succinic Acid $C_5H_8O_4$.—To prepare this acid from tartaric acid the latter is mixed with an equal weight of finely powdered pumice-stone and distilled. On evaporating the distillate the acid is obtained in transparent crystals melting at 112°; at a higher temperature it is resolved into water and *pyrotartaric anhydride* $C_5H_2O_3$.

On heating propene dibromide with potassium cyanide and spirits of wine, the nitrile of pyrotartaric acid is obtained. Pyrotartaric acid is also produced by boiling β cyanobutyric acid with an alkali:—

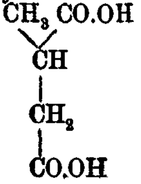
Propene Dicyanide.



β Cyanobutyric Acid.

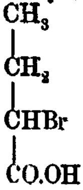


Pyrotartaric Acid.

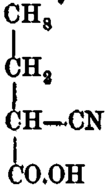


Ethylmalonic Acid $C_5H_8O_4$.—When α bromobutyric acid is heated with alcohol and potassium cyanide, and the product thus formed boiled with potash solution, the potassium salt of ethylmalonic acid is obtained:—

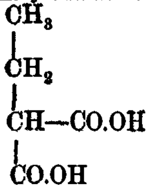
α Bromobutyric Acid.



α Cyanobutyric Acid.



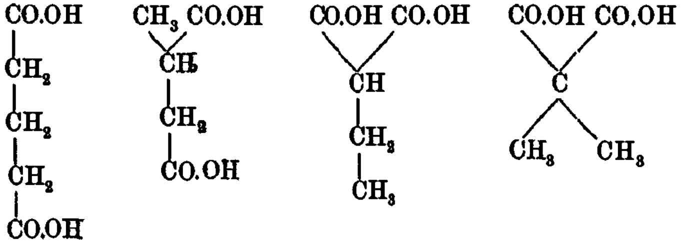
Ethylmalonic Acid.



Ethylmalonic acid crystallizes in colourless prisms resembling pyrotartaric acid, and melting like the latter at 112°. Both acids can, however, easily be distinguished by heating them; pyrotartaric yields a crystalline sublimate of the anhydride, whilst ethylmalonic acid is completely resolved into carbon dioxide and butyric acid, the former acid being methylsuccinic acid, and the latter methylisosuccinic acid.

Glutamic Acid $C_3H_5(NH_2)\left\{\begin{matrix}CO.OH\\CO.OH\end{matrix}\right.$, a homologue of aspartic acid, is produced, together with the latter body and other compounds, by boiling legumin and conglutin (see Albuminous Principles) with dilute sulphuric acid. It crystallizes in rhombic tetrahedrons, and is converted by the action of nitrous acid into *glutanic acid* $C_3H_5(OH)(CO_2H)$, an indistinctly crystalline mass, forming amorphous salts.

Deoxyglutanic Acid $C_3H_6\left\{\begin{matrix}CO.OH\\CO.OH\end{matrix}\right.$ is produced by heating glutanic acid with concentrated hydriodic acid to 120°. It is very readily soluble in water, and forms large, transparent, monoclinic crystals melting at 97°, and decomposing above 280° into water and the anhydride $C_5H_6O_3$. This reaction explains the constitution of deoxyglutanic acid, and shows that it is a normal compound, because only four isomerides having the formula $C_3H_6(CO_2H)_2$ can exist, viz.:—



The second of these formulæ represents the constitution of pyrotartaric acid, and the third that of ethylmalonic acid; deoxyglutanic acid must therefore have either the constitution represented by formula 1 or 4. But an acid of this composition having linked two carboxyls to the same carbon atom would on heating (analogous to ethylmalonic acid) be resolved into carbon dioxide and isobutyric acid, whilst deoxyglutanic acid yields an anhydride and water, from which it follows that it must have the constitution assigned to it.

COMPOUNDS CONTAINING MORE THAN FIVE ATOMS OF CARBON.

Hexene or Hexylene C_6H_{12} occurs in the light oils from boghead and cannel-tar, and is readily formed by heating the secondary chloride or iodide of hexyl with alcoholic potash; it boils at 70°. *Hexene glycol* $C_6H_{12}(OH)_2$ is a thick liquid boiling at 207°.

Heptene or Heptylene C_7H_{14} occurs in the same oils in which hexene is found, and has been obtained from secondary heptyl chloride. The same hydrocarbon is formed by acting on œnanthaldehyde with phosphorus pentachloride and decomposing the *œnanthidene chloride* $C_7H_{14}Cl_2$ thus formed with sodium. It boils at 100°.

Octene or Octylene C_8H_{16}, a liquid boiling at 125°, is found together with its lower homologues, and is readily obtained by distilling methyl-hexyl carbinol with zinc chloride. Octene glycol $C_8H_{16}(OH)_2$ is insoluble in water and boils at 235° to 240°.

Diamylene $C_{10}H_{20}$.—To prepare this hydrocarbon one volume of amylene is shaken with two volumes of a mixture, consisting of two volumes of concentrated sulphuric acid and one volume of water, in stoppered cylinders which are surrounded by ice-cold water. It boils at 160°. On heating it with a solution of potassium dichromate in dilute sulphuric acid, it is oxidized to *diamylene oxide* $C_{10}H_{20}O$, a mobile light liquid boiling between 180° to 190°, and possessing a strong smell like camphor. On further oxidation it yields carbon dioxide, acetic acid, and *amethenic acid* $C_7H_{14}O_2$, an oily liquid, which is isomeric with œnanthylic acid, from which it differs however by exhibiting only very feeble acid properties.

Cetene $C_{16}H_{32}$ is produced by the distillation of cetyl alcohol with phosphorus pentoxide, and also by the destructive distillation of spermaceti. It is an oily liquid, boiling at 275°. *Cetene dibromide* $C_{16}H_{32}Br_2$ is a heavy non-volatile liquid. When cetene is shaken with a dilute solution of hypochlorous acid, they combine forming *cetene chlorhydrate* $C_{16}H_{32}\left\{\begin{matrix}Cl\\OH\end{matrix}\right.$, a liquid boiling at about 300°, and yielding by the action of caustic potash, *cetene oxide* $C_{16}H_{32}O$, colourless needles which are insoluble in water.

Cerotene $C_{27}H_{54}$, a crystalline solid, has been obtained by the destructive distillation of Chinese wax.

Melene $C_{30}H_{60}$ is produced by subjecting bees-wax to distillation; it crystallizes from hot alcohol in scales, melting at 62°.

LEUCIC ACID AND LEUCINE.

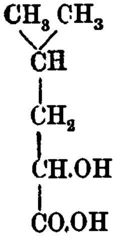
Leucine or Amido-isocaproic Acid $C_6H_{11}(NH_2)O_2$ occurs in several parts of the animal organism, and is formed in certain diseases in considerable quantity. It is also produced by the decomposition of animal substances such as glue, horn, and proteids, and during putrefaction, and is therefore contained in old cheese. It is readily obtained by boiling horn-turnings with dilute sulphuric acid, and has also been produced artificially by boiling valeraldehyde with prussic acid and hydrochloric acid, as well as by the action of ammonia upon monobromo-isocaproic acid.

It crystallizes in white shining scales, which are but little soluble in cold water, and still less so in alcohol. It melts at 170°, and at a higher temperature it is resolved into carbon dioxide and amylamine. On fusing it with caustic potash, it yields potassium carbonate, ammonia, and potassium valerate. By heating it with fuming hydriodic acid it is converted into isocaproic acid.

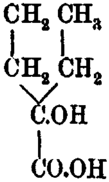
By dissolving it in dilute nitric acid, and passing nitric trioxide into this solution, nitrogen is given off, and *leucic acid* $C_6H_{11}(OH)O_2$ is formed, crystallizing in needles, melting at 73°, and subliming readily below 100°.

By the action of zinc and ethyl iodide upon ethyl oxalate an acid isomeric with leucic acid, called *diethoxalic acid*, has been obtained. It crystallizes in large prisms melting at 74°·5. The isomerism of leucic acid and diethoxalic acid is explained by the following formulæ:—

Leucic Acid.



Diethoxalic Acid.



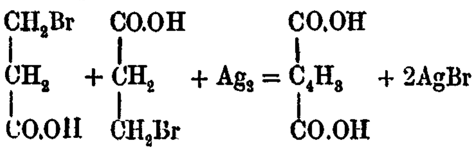
Whether the leucins of different origin are identical, or whether perhaps some are derived from normal valerianic or pentylic acid, is a question which has yet to be decided.

ACIDS OF THE SERIES $C_nH_{2n-2}O_4$.

The acids of this series containing more than 5 atoms of carbon are formed, together with succinic acid, by oxidizing fats with nitric acid. From the mixture thus obtained pure acids cannot be isolated by recrystallization from water, but they may be separated by means of ether, in which some are much more soluble than others.

The same acids are formed by the action of fuming nitric acid upon the acids of the series $C_nH_{2n-4}O_4$, which will be described further on.

Adipic Acid $C_6H_{10}O_4$ is conveniently prepared by boiling sebacic acid with nitric acid, and recrystallizing the product from water to remove succinic acid. The same compound has been produced by heating β bromopropionic acid with silver-dust:—

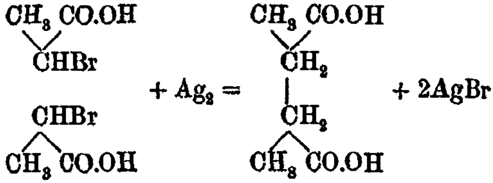


$$\begin{array}{lclclcl} CH_2Br & & CO.OH & & & CO.OH & \\ | & & | & & & | & \\ CH_2 & + & CH_2 & + Ag_2 & = & C_4H_8 & + 2AgBr \\ | & & | & & & | & \\ CO.OH & & CH_2Br & & & CO.OH & \end{array}$$

It crystallizes in shining prisms, melting at 148°, and is readily soluble in boiling water, but only sparingly in cold water.

When one molecule of adipic acid is heated with two molecules of bromine to 160°, *monobromadipic acid* $C_6H_9BrO_4$ is formed, which by the action of caustic potash is transformed into *adipomalic acid* $C_4H_7(OH)(CO.OH)_2$, a body resembling malic acid. By heating adipic acid with four molecules of bromine, *dibromadipic acid* is produced, a very unstable compound, which, when heated with water to 150°, yields *adipotartaric acid* $C_4H_6(OH)_2(CO.OH)_2$, crystallizing in thin monoclinic plates. It resembles tartaric acid, forming an acid potassium salt, which is but sparingly soluble in water.

Dimethylsuccinic Acid $C_6H_{10}O_4$ has been obtained by the action of silver-dust on *a* bromopropionic acid:—



On evaporating its solution it is left behind as a colourless syrupy liquid.

Pimelic Acid $C_7H_{12}O_4$.—There are some doubts whether this acid exists among the oxidation-products of fats, but it has been obtained by fusing camphoric acid $C_8H_{14}(CO_2H)_2$ with caustic potash. It is crystalline, and melts at 114°.

Suberic Acid $C_8H_{14}O_4$ was first obtained by oxidizing cork with nitric acid. It can be easily obtained in quantity by boiling castor-oil with nitric acid, fusing the resulting solid mass, and exhausting it with cold ether, in which suberic acid is scarcely soluble. It crystallizes from a boiling aqueous solution in long needles or plates, melting at 140°. When heated with caustic baryta it yields *hexane*, besides other products:—

$$C_6H_{12}\left\{\begin{matrix}CO.OH\\CO.OH\end{matrix}\right. = C_6H_{14} + 2CO_2$$

By the same reactions by which succinic acid is converted into malic acid and tartaric acid, suberic acid has been transformed into *subcromalic acid* $C_6H_{11}(OH)(CO.OH)_2$ and *suberotartaric acid* $C_6H_{10}(OH)_2(CO.OH)$, which are both very soluble in water, and do not crystallize.

Azelaic Acid $C_9H_{16}O_4$ is formed, together with suberic acid, by oxidizing castor-oil. It is readily soluble in cold ether, sparingly in cold water, and more freely in boiling water. It crystallizes in large, thin, shining plates or needles, melting at 106°. On heating with caustic baryta it yields *heptane* C_7H_{16}.

Sebacic Acid $C_{10}H_{18}O_4$ is obtained, together with methyl-hexyl carbinol, by fusing castor-oil soap with caustic alkalis, and it is also produced by oxidizing spermaceti with nitric acid. It forms shining plates, melting at 128°. It is less soluble in ether than azelaic acid, but more than suberic acid.

Brassic Acid $C_{11}H_{20}O_4$ has only been produced by heating behenoleic acid $C_{22}H_{40}O_2$ with fuming nitric acid :—

$$C_{22}H_{40}O_2 + 3O_2 = 2C_{11}H_{20}O_4$$

It is sparingly soluble in water, forming scaly crystals, melting at 108°·5.

Rocellic Acid $C_{17}H_{32}O_4$ occurs in different species of lichen (*Rocella tinctoria, R. fuciformis,* &c.). To prepare it, the lichens are exhausted with ammonia, the solution is precipitated with calcium chloride, and the precipitate of calcium rocellate decomposed by hydrochloric acid. Rocellic acid is insoluble in water, but readily soluble in alcohol and ether, and crystallizes in prisms melting at 132°.

CITRIC ACID $C_6H_8O_7$.

This tribasic acid occurs in the juice of lemons, of currants and gooseberries, and other kinds of fruit. It is manufactured from lemon-juice, which is allowed to ferment in order that mucilage and other bodies may separate out. The liquid is then heated to the boiling-point, filtered, and neutralized with chalk and a little milk of lime. The insoluble calcium citrate is well washed and decomposed by sulphuric acid. Citric acid crystallizes in large, transparent, rhombic prisms, possessing an agreeable sour taste.

CITRATES.

The citrates of the alkali-metals are soluble in water. They form three series :—

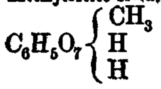
$$C_6H_5O_7\left\{\begin{matrix}K\\H\\H\end{matrix}\right. \qquad C_6H_5O_7\left\{\begin{matrix}K\\K\\H\end{matrix}\right. \qquad C_6H_5O_7\left\{\begin{matrix}K\\K\\K\end{matrix}\right.$$

Calcium Citrate $(C_6H_5O_7)_2Ca_3$ is a white crystalline powder which is sparingly soluble in cold water, and still less in boiling water. On neutralizing citric acid in the cold with lime-water, no precipitate is formed; but on boiling the liquid, calcium citrate separates out, which on cooling slowly redissolves. It is freely soluble in a solution of citric acid, forming the acid salt $C_6H_5O_7\left\{\begin{matrix}Ca\\H\end{matrix}\right. + H_2O$, which crystallizes in shining plates.

Silver Citrate $C_6H_5O_7Ag_3$ is a white flocculent precipitate, which can be crystallized from boiling water.

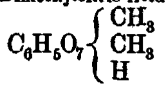
Methyl Citrates.—On passing hydrochloric acid gas into a solution of citric acid in methyl alcohol, the following compounds are formed, which are all crystalline solids:—

Methylcitric Acid.



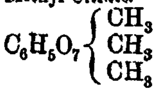
$$C_6H_5O_7\left\{\begin{matrix}CH_3\\H\\H\end{matrix}\right.$$

Dimethylcitric Acid.



$$C_6H_5O_7\left\{\begin{matrix}CH_3\\CH_3\\H\end{matrix}\right.$$

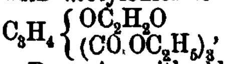
Methyl Citrate.



$$C_6H_5O_7\left\{\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\right.$$

Ethyl Citrate $C_6H_5O_7(C_2H_5)_3$ is an oily, non-volatile liquid.

Citric acid contains one alcoholic hydroxyl, and forms consequently also ethers with acid radicals. Thus, on treating ethyl citrate with acetylchloride the ethyl-ether of *acetylcitric acid* is formed,



$C_3H_4\left\{\begin{matrix}OC_2H_3O\\(CO.OC_2H_5)_3\end{matrix}\right.$, a liquid boiling at 288°.

By acting with chlorine or bromine upon an aqueous solution of the acid or a citrate, decomposition takes place with the formation of chloroform or bromoform, and substitution-products of methyl acetate.

Citric acid melts at 150°, and is resolved at 175° into water and aconitic acid:—

$$C_6H_8O_7 = H_2O + C_6H_6O_6$$

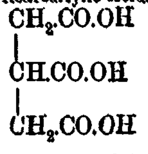
ACONITIC ACID $C_6H_6O_6$.

This tribasic acid occurs in several plants (*Aconitum Napellus, Delphinium consolidum,* and *Equisetum fluviatile*). It is best prepared by heating citric acid quickly until oily drops begin to condense in the neck of the retort. The residue is exhausted with ether, in which aconitic acid dissolves. It forms crystalline grains, readily soluble in water, and possessing a strong acid taste.

By the action of sodium amalgam upon its aqueous solution it is converted into tribasic *tricarballylic acid* $C_6H_8O_6$, which is also obtained by heating propenyl tribromide $C_3H_5Br_3$ (see Glycerin) with potassium cyanide, and decomposing the nitrile thus formed with caustic potash.

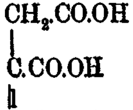
These reactions explain the constitution of these three acids:—

Tricarballylic Acid.



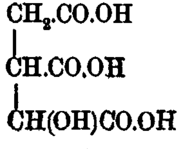
$$\begin{array}{l}CH_2.CO.OH\\|\\CH.CO.OH\\|\\CH_2.CO.OH\end{array}$$

Aconitic Acid.



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

Citric Acid.



$$\begin{array}{l}CH_2.CO.OH\\|\\CH.CO.OH\\|\\CH(OH)CO.OH\end{array}$$

Itaconic Acid $C_5H_2O_4$ is formed by distilling aconitic acid:—

$$C_6H_6O_6 = CO_2 + C_5H_6O_4$$

It is readily obtained by heating citric acid rapidly until the distillate begins to assume a dark colour. The liquid thus obtained is heated to 120°, and the crystals which form on cooling are recrystallized from water. It is also formed by heating an aqueous solution of citric acid in closed tubes to 160°. It forms large rhombic prisms possessing a sour taste. It melts at 161°, and is decomposed by distillation into water and the *anhydride of citraconic acid.*

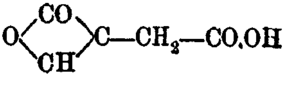
Citraconic Acid is isomeric with itaconic acid, and is obtained by repeatedly distilling the latter acid; *citraconic anhydride* $C_5H_4O_3$ being formed, an oily liquid, which when exposed to the air absorbs moisture, and is converted into citraconic acid, forming rhombic octahedrons melting at 120°. On heating it with water to 120° it is again converted into itaconic acid.

Mesaconic Acid.—When itaconic acid is boiled with weak nitric acid, a new isomeric modification is formed, which crystallizes from alcohol in shining prisms, which are sparingly soluble in water, melt at 208°, and sublime at a higher temperature.

These three isomeric acids are non-saturated compounds which combine with nascent hydrogen, all three yielding one and the same product, viz. *pyrotartaric acid* $C_3H_6\left\{\begin{matrix}CO.OH\\CO.OH\end{matrix}\right.$. To explain the isomerism of itaconic, citraconic, and mesaconic acids $C_3H_4\left\{\begin{matrix}CO.OH\\CO.OH\end{matrix}\right.$ we must assume that in the propene group C_3H_6 of pyrotartaric acid, two atoms of hydrogen are wanting, occupying different positions. This is proved by the fact that the three acids, on combining with bromine or with hydrochloric acid, yield isomeric substitution-products of pyrotartaric acid.

Bibromopyrotartaric Acid $C_3H_4Br_2(CO.OH)_2$ is obtained by adding bromine to an aqueous solution of itaconic acid. On heating it with water and silver oxide it is converted into an acid which, being homologous with tartaric acid, has been called *itatartaric acid* $C_3H_4(OH)_2(CO.OH)_2$. By boiling an aqueous solution of sodium bibromopyrotartarate it is resolved into sodium bromide and *aconic acid* $C_5H_4O_4 = C_3H_2(CO.OH)_2$.

This acid forms large crystals melting at 154°; it is a monobasic acid. On boiling it with baryta-water it is resolved into formic acid and succinic acid. It is not acted upon by heating it with acetic anhydride, showing that it contains no hydroxyl, and has probably the following constitution:—



Citrabibromopyrotartaric Acid $C_3H_4Br_2(CO.OH)_2$ is obtained by combining bromine with citraconic acid. It is readily soluble in water, and yields, on boiling its solution with potash, potassium bromide, potassium carbonate, and *monobromo-isocrotonic acid* $C_4H_5BrO_2$.

Mesabibromopyrotartaric Acid $C_3H_4Br_2(CO.OH)_2$.—Mesaconic acid combines readily with bromine, yielding this acid, which by the action of alkalis is also converted into monobromo-isocrotonic acid. By the action of sodium amalgam and water on monobromo-isocrotonic acid it is converted into *isobutyric acid.*

Monochloropyrotartaric Acid $C_3H_5Cl(CO.OH)_2$ is produced by heating itaconic acid with concentrated hydrochloric acid. It melts at 140°, and yields, when heated with water, *itamalic acid* $C_3H_5(OH)(CO.OH)_2$, long, white, deliquescent needles, which when strongly heated are resolved into water and itaconic acid.

Citramonochloropyrotartaric Acid $C_3H_5Cl(CO.OH)_2$.—This compound, which is formed by heating citraconic acid with hydrochloric acid, is a very unstable body, easily splitting up into hydrochloric and mesaconic acids. On heating its solution with an alkali it is resolved into carbon dioxide, hydrochloric acid, and isocrotonic acid.

Mesamonochloropyrotartaric Acid is a more stable body than the preceding acid, but yields by the action of water and alkalis the same products as the latter.

Monochlorocitramalic Acid $C_3H_4(OH)Cl(CO.OH)_2$ is an amorphous substance formed by the union of citraconic acid with hypochlorous acid. On heating its aqueous solution with zinc, amorphous and deliquescent *citramalic acid* $C_3H_5(OH)(CO.OH)_2$ is obtained. When the neutral solution of a monochlorocitramalate is boiled, *citratartaric acid* $C_3H_4(OH)_2(CO.OH)_2$ is formed.

DEOXALIC ACID $C_6H_8O_9$.

The ethyl-ether of this acid is produced by shaking ethyloxalate with sodium amalgam at a low temperature. The resulting soft grey mass is exhausted with ether, which dissolves ethyl desoxalate, whilst the residue contains mercury, sodium oxalate, and other undefined bodies.

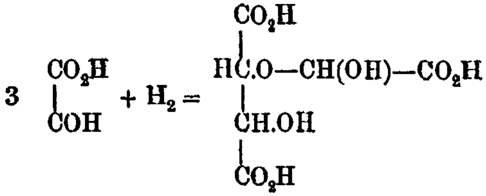
Ethyl Deoxalate $C_6H_5O_9(C_2H_5)_3$ is soluble in water, and forms large transparent crystals. On boiling it with baryta-water it is converted into *barium deoxalate* $C_6H_4Ba_2O_9 + 3H_2O$, a white amorphous powder. *Ammonium deoxalate* $C_6H_5(NH_4)_3O_9 + H_2O$ is obtained by decomposing the barium-salt with ammonium carbonate. By adding silver nitrate to its solution, *silver deoxalate* $C_6H_4Ag_4O_9 + H_2O$ is precipitated, a very unstable body, which, when exposed in the moist state to the daylight, decomposes, silver separating out in form of a mirror.

The free deoxalic acid is not known. On decomposing the silver salt with hydrogen sulphide, and evaporating the solution, the acid is resolved into glyoxylic acid and inactive tartaric acid:—

$$C_6H_8O_9 = C_4H_6O_6 + C_2H_2O_3$$

By the action of acetic acid upon potassium deoxalate the compound $C_5H_4K_2O_8 + H_2O$ is produced. The corresponding acid $C_6H_0O_8$ is tribasic, and can be obtained by decomposing the lead salt with hydrogen sulphide; it is a crystalline deliquescent mass.

The formation of deoxalic acid from oxalic acid can be easily explained. The latter acid is first reduced to glyoxylic acid, of which three molecules combine with hydrogen, forming deoxalic acid:—



$$3\begin{array}{l}CO_2H\\ |\\ COH\end{array} + H_2 = \begin{array}{l}CO_2H\\ |\\ HC.O-CH(OH)-CO_2H\\ |\\ CH.OH\\ |\\ CO_2H\end{array}$$

This formula explains the decomposition of the acid into tartaric and glyoxylic acids. Deoxalic acid is tribasic, but as the barium and silver salt show, one atom of hydrogen in one of the alcoholic hydroxyl groups can also be replaced by a metal.

URIC ACID $C_5H_4N_4O_3$.

Uric acid occurs in the urine of all animals. The excrements of serpents consist almost entirely of uric acid and ammonium urate, and those of birds and insects contain a large quantity of these compounds. Human urine, and that of animals feeding on flesh or corn, contain only a small quantity of uric acid, and still less is found in the urine of herbivorous animals.

Being very sparingly soluble it often separates from urine as a crystalline precipitate; if this takes place in the bladder, gravel and stones are produced. In certain diseases, as in gout, acid sodium urate crystallizes out in the muscles and between the joints.

For the preparation of uric acid either guano or excrements of serpents are used. The excrements, or guano which has been previously treated with dilute hydrochloric acid, are dissolved in dilute hot potash-solution, and the uric acid precipitated by dilute sulphuric acid.

Uric acid is a white crystalline powder, without taste and smell; it is almost insoluble in cold water, and only sparingly in boiling water. In alcohol and ether it is insoluble, but it is readily soluble in hot concentrated sulphuric acid, and separates out again from this solution on addition of water.

URATES.

Uric acid is a bibasic acid. The normal salts of the alkali-metals are not very freely soluble in water; the most soluble being lithium urate; potassium urate is less soluble, and sodium urate the least soluble salt. By passing carbon dioxide into their solutions, acid urates are precipitated, being less soluble than the normal salts. The urates of the other metals are insoluble.

Uric acid can easily be detected, even when present in small quantity, by dissolving it in a few drops of nitric acid, and evaporating the solution cautiously nearly to dryness. A yellow residue is obtained, which assumes a deep-red colour on addition of ammonia (see Murexide).

By destructive distillation uric acid yields cyanuric acid, ammonium cyanide, urea, and other products.

On heating it with hydriodic acid to 160° to 170° it is resolved into glycocoll, ammonia, and carbon dioxide:—

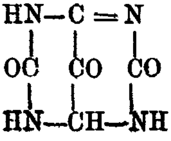
$$C_5H_4N_4O_3 + 5H_2O = C_2H_5NO_2 + 3NH_3 + 3CO_2$$

By the action of cold nitric acid it is oxidized to alloxan and urea:—

$$C_5H_4N_4O_3 + O + H_2O = C_4H_2N_2O_4 + CH_4N_2O$$

Alloxan $C_4H_2N_2O_4$ is mesoxalyl-urea, *i.e.* urea in which two atoms of hydrogen are replaced by the dyad radical mesoxalyl C_3O_3.

This reaction shows that uric acid contains three atoms of carbon linked together. Its constitution is not yet exactly understood; the following formula does not appear improbable, as it explains most of the reactions and decompositions of this acid:—



Uric acid is remarkable for the facility with which it is altered by oxidizing agents, and for the great number of interesting derivatives which it thus yields. Most of these ureids are compound ureas or urea in which a part of the hydrogen is replaced by acid radicals.

Mycomelic Acid $C_4H_4N_4O_2$.—When uric acid is heated with water in sealed tubes to 180°, mycomelic acid is formed. This compound is of great interest, as it has lately been obtained by a very simple synthetical process. Equal volumes of cyanogen gas and ammonia combine, forming a black amorphous body called *hydrazulmin* $C_4H_6N_6$;

by acting on it with water it is converted into *hydrazulmoxin* or *azulmic acid* $C_4H_5N_5O$:—

$$C_4H_6N_6 + H_2O = C_4H_5N_5O + NH_3$$

This compound is also produced by the spontaneous decomposition of an aqueous solution of cyanogen gas, and by the action of this gas on aqueous ammonia. When azulmic acid is boiled repeatedly with water, it is converted into mycomelic acid :—

$$C_4H_5N_5O + H_2O = C_4H_4N_4O_2 + NH_3$$

Mycomelic acid is a light yellow powder, very sparingly soluble in cold water, and little more in boiling water. In acids and alkalis it is freely soluble. Its aqueous yellow solution shows a fine greenish blue fluorescence, and when dropped into water forms beautiful sky-blue clouds.

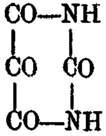
Alloxan or Mesoxalyl-urea $C_4H_2N_2O_4$.—Cold nitric acid dissolves uric acid with evolution of carbon dioxide and nitrogen, and when the solution is saturated it solidifies to a crystalline mass of alloxan. Alloxan crystallizes from a warm aqueous solution in crystals resembling heavy spar, and containing four molecules of water. From a hot concentrated solution it separates on evaporation in hard rhombic crystals, containing only one molecule of water. Its aqueous solution stains the skin red, and confers on it a nauseous smell. It possesses an unpleasant sour-salty taste, and an acid reaction. With ferrous salts it gives a blue coloration. When alloxan is boiled with ammonia it is converted into mycomelic acid :—

$$C_4H_2N_2O_4 + 2NH_3 = C_4H_4N_4O_3 + 2H_2O$$

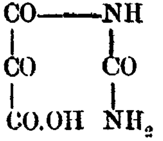
Alloxanic Acid $C_4H_4N_2O_5$.—The salts of this acid are produced by the action of alkalis upon alloxan. It is conveniently prepared by heating a solution of alloxan and barium chloride with potash solution, which has to be added gradually until the precipitate formed does not longer redissolve. On cooling, barium alloxanate separates out as a crystalline powder, which is decomposed by sulphuric acid. The acid is readily soluble in water, and crystallizes in white needles.

Mesoxalic Acid $C_3H_2O_5$.—When barium alloxanate is boiled with a large quantity of water it is resolved into urea and barium mesoxalate. This reaction will be easily understood by comparing the following formulæ :—

Alloxan.

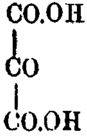


Alloxanic Acid.



$$\begin{array}{ll} CO & \!\!\!-\!\!-NH \\ | & \quad | \\ CO & \quad CO \\ | & \quad | \\ CO.OH & \quad NH_2 \end{array}$$

Mesoxalic Acid.

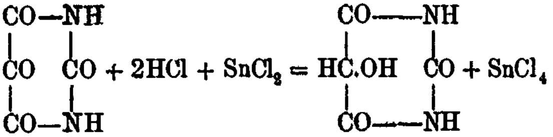


$$\begin{array}{l} CO.OH \\ | \\ CO \\ | \\ CO.OH \end{array}$$

Mesoxalic acid forms deliquescent crystals. By the action of nascent hydrogen it is converted into tartronic acid (see page 228). Silver mesoxalate is an insoluble precipitate, which when boiled with water is decomposed into free mesoxalic acid, silver oxalate, carbon dioxide, and metallic silver :—

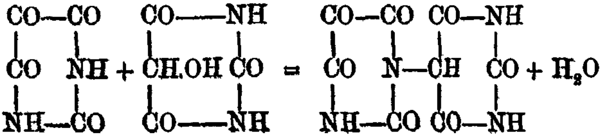
$$2C_3O_5Ag_2 + H_2O = C_3O_5H_2 + C_2O_4Ag_2 + CO_2 + Ag_2$$

Dialuric Acid or Tatronyl-urea $C_4H_4N_2O_4$ is produced by the action of reducing agents upon alloxan; thus it is formed by mixing hot solutions of stannous chloride, hydrochloric acid, and alloxan :—



It crystallizes in short, four-sided prisms, and has a strong acid reaction; when exposed to the air it absorbs oxygen, and is converted into alloxantin.

Alloxantin $C_8H_4N_4O_7$.—This body is formed not only by the oxidation of dialuric acid, but also by reducing alloxan with hydrogen sulphide. It is a compound standing intermediate between dialuric acid and alloxan, and is therefore also obtained, as a crystalline precipitate, by mixing concentrated solutions of these two compounds :—

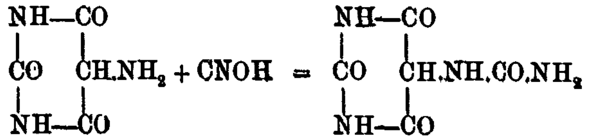


It crystallizes in small hard prisms containing three molecules of water. When exposed to the air it absorbs ammonia and assumes a reddish colour. Its aqueous solution gives with baryta-water a violet precipitate, which when boiled with water is resolved into barium dialurate and alloxanate.

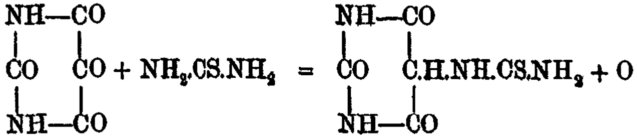
Uramile or Dialuramide $C_4H_5N_3O_3$.—When alloxantin is boiled with a solution of ammonium chloride, uramile is deposited as a crystalline precipitate, and the solution contains alloxan :—

$$C_8H_4N_4O_7 + NH_3 = C_4H_5N_3O_3 + C_4H_2N_2O_4$$

Pseudo-uric Acid $C_5H_2N_4O_4$.—The potassium salt of this acid is obtained as a yellow crystalline powder, when uramile is boiled with a concentrated solution of potassium cyanate. The free acid forms small colourless crystals, sparingly soluble in water. The following equation explains the formation of this body :—



Sulpho-pseudo-uric Acid $C_5H_6N_4O_3S$ is produced by heating alloxan and sulphur-urea with a concentrated alcoholic solution of sulphur dioxide:—



It forms thin white needles and is insoluble in water, but soluble in acids.

Purpuric Acid $C_8H_5N_5O_6$.—This compound is not known in the free state; its ammonium salt is that beautiful substance known by the name of *murexide*, which is obtained by boiling a mixture of dialuramide and mercuric oxide with dilute aqueous ammonia. It may also be prepared by adding ammonia to a hot solution of dialuramide and alloxan:—

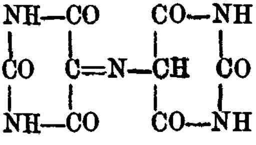
$$NH_3 + C_4H_5N_3O_3 + C_4H_2N_2O_4 = C_8H_5N_5O_7.NH_3 + H_2O$$

Murexide is also formed by evaporating uric acid with a little nitric acid nearly to dryness, and adding ammonia to the residue.

Murexide crystallizes in small prisms, which by reflected light exhibit a fine beetle-green lustre, and dissolve in water with an intense purple colour. The solution dyes silk and wool a beautiful red shade, and was a few years ago manufactured for this purpose, but has now been superseded by aniline-red.

When a solution of murexide is boiled with potassium nitrate, *potassium purpurate* $C_8H_4N_5O_6K$ is formed, a salt resembling murexide. The purpurates of the alkali-metals dissolve in water with a bluish-purple colour; those of the other metals are insoluble in water. They are decomposed by acids with the formation of dialuramide and alloxan.

Purpuric acid has probably the following constitution:—



Hydurilic Acid $C_8H_4N_4O_6$.—When dialuric acid is heated with glycerin it is resolved into carbon dioxide, formic acid, and acid ammonium hydurilate. The free acid, which may be obtained by decomposing the ammonium-salt with hydrochloric acid, crystallizes in small four-sided prisms, and is sparingly soluble in water. It is a strong bibasic acid, which, as well as its salts, give with ferric chloride a beautiful green coloration. Concentrated nitric acid oxidizes it to alloxan; a more dilute acid produces, besides the latter compound, two other bodies, called violuric acid and dilituric acid.

Violuric Acid or Nitrosomalonyl-urea $CH(NO)\left\{\begin{matrix}CO.NH\\CO.NH\end{matrix}\right\}CO$.—By the action of cold dilute nitric acid (1·2 specific gravity) upon hydurilic acid, alloxan and violuric acid are formed:—

$$C_8H_6N_4O_6 + HNO_3 = C_4H_2N_2O_4 + C_4H_3N_3O_4 + H_2O$$

The potassium salt of this acid is obtained by adding acetic acid to a mixture of hydurilic acid and potassium nitrite; it crystallizes in deep-blue plates having the composition $C_4H_2N_3O_4K + 2H_2O$. When barium chloride is added to the violet solution of potassium violurate, the barium salt is obtained as a red precipitate. The free violuric acid is prepared by decomposing the latter salt with sulphuric acid; it crystallizes in yellowish prisms. All its salts are distinguished by their beautiful colours. Ammonium violurate resembles the potassium salt; sodium violurate crystallizes in short red needles; magnesium violurate forms small purple crystals; and the ferrous salt crystallizes in hexagonal plates, having a red metallic lustre and dissolving in water with a blue colour.

When bromine is added to a solution of violuric acid, nitrous fumes are given off, and *bibromomalonyl-urea* $C_4H_2Br_2N_2O_3$ is formed. Caustic potash decomposes violuric acid into urea, and nitrosomalonic acid.

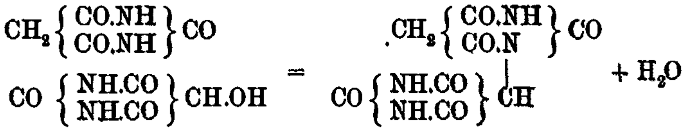
Nitrosomalonic Acid $CH(NO)\left\{\begin{matrix}CO.OH\\CO.OH\end{matrix}\right.$ is very soluble in water, and crystallizes in glistening needles. When heated it first fuses and afterwards decomposes with a violent explosion. By the action of sodium amalgam on its aqueous solution it is converted into *amidomalonic acid* $CH(NH_2)\left\{\begin{matrix}CO.OH\\CO.OH\end{matrix}\right.$.

Hydriodic acid converts violuric acid into *dialuramide* or *amidomalonyl-urea.*

Dilituric Acid or Nitromalonyl-urea $CH(NO_2)\left\{\begin{matrix}CO.NH\\CO.NH\end{matrix}\right\}CO$ is formed by the action of nitric acid upon violuric acid or hydurilic acid. It crystallizes in colourless prisms and forms colourless salts. Hydriodic acid reduces it to dialuramide.

Barbituric Acid or Malonyl-urea $CH_2\left\{\begin{matrix}CO.NH\\CO.NH\end{matrix}\right\}CO$ is obtained by reducing bibromomalonyl-urea with hydriodic acid or sodium amalgam and water. It is a bibasic acid, crystallizing in rhombic crystals which are sparingly soluble in water. On boiling with potash solution it is resolved into malonic acid and urea.

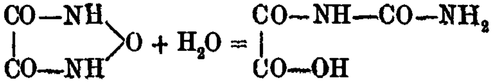
Hydurilic acid, a compound previously described, is nearly related to barbituric acid. It is formed from two molecules of dialuric acid, one of them being converted into barbituric acid, which combines with another molecule thus:—



$$\begin{matrix} CH_2\left\{\begin{matrix}CO.NH\\CO.NH\end{matrix}\right\}CO & & CH_2\left\{\begin{matrix}CO.NH\\CO.N\end{matrix}\right\}CO & \\ & = & & + H_2O \\ CO\left\{\begin{matrix}NH.CO\\NH.CO\end{matrix}\right\}CH.OH & & CO\left\{\begin{matrix}NH.CO\\NH.CO\end{matrix}\right\}CH & \end{matrix}$$

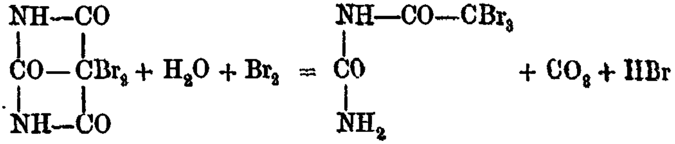
Parabanic Acid or Oxalyl-urea $C_2O_2\left\{\begin{matrix}NH\\NH\end{matrix}\right\}CO$ is formed by oxidizing alloxan, and is readily obtained by dissolving uric acid in common nitric acid, and evaporating the solution to the consistency of a syrup. It crystallizes in thin plates, readily soluble in water, and possessing a very sour taste. It is a bibasic acid, which when boiled with diluted acids is resolved into urea and oxalic acid. Its aqueous solution gives with silver nitrate a white precipitate of silver parabanate $C_3N_2O_3Ag_2$, which when heated with methyl iodide yields oxalyl-dimethylurea $C_3N_2O_3(CH_3)_2$, a compound which has been also obtained as a product of decomposition of caffeine.

The aqueous solutions of parabanates soon undergo a change, parabanic acid combining with water and forming *oxaluric acid* $C_3H_4N_2O_4$:—

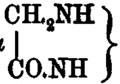


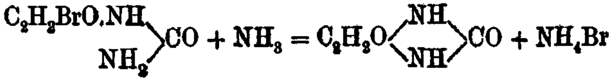
Oxaluric acid is a crystalline powder, and is sparingly soluble in water. *Ethyl oxalurate* has been produced by the action of ethyl-oxalyl chloride (see page 204) upon urea. It forms a crystalline powder, which is but sparingly soluble in cold water.

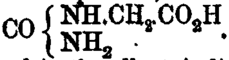
Tribromacetyl-urea $C_3H_3Br_3N_2O_2$ is obtained by the action of bromine upon an aqueous solution of bibromomalonyl-urea:—



It crystallizes in long colourless needles, the dust of which has a most irritating action upon the nose and eyes. It fuses at 148°, and at a higher temperature decomposes into tribromacetamide and cyanuric acid. By the action of alkalis it is resolved into urea, carbon dioxide, and bromoform.

Hydantoïn or Glycolyl-urea  $\left.\begin{matrix} CH_2NH \\ | \\ CO.NH \end{matrix}\right\} CO$.—When urea is acted upon by monobromacetyl bromide, monobromacetyl urea is formed, a compound resembling tribromacetyl-urea. On heating this body with alcoholic ammonia it is converted into hydantoïn:—

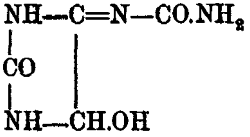


The same body is formed, together with carbon dioxide, water, and free iodine, when alloxan is heated with hydriodic acid. It forms colourless crystals, possessing a faint sweet taste, and melting at 206°. By boiling with baryta-water it takes up water, and is converted into *hydantoic acid* or *glycoluric acid*  $CO\left\{\begin{matrix} NH.CH_2.CO_2H \\ NH_2 \end{matrix}\right.$.

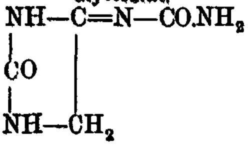
Allantoïn $C_4H_6N_4O_3$ is contained in the allantoic liquid or urine of the fœtal calf, and also in the urine of sucking calves. It is also produced, together with oxalic acid and urea, by heating uric acid with lead dioxide and water. It forms brilliant, transparent prisms, which are sparingly soluble in water.

By the action of sodium amalgam and water it is converted into *glycolurile* $C_4H_6N_4O_2$, which, when heated with acids, takes up water, and is resolved into urea and glycolyl-urea. The constitution of these compounds may therefore be expressed as follows:—

Allantoïn.



Glycolurile.



XANTHINE, SARCINE, AND GUANINE.

Xanthine	$C_5H_4N_4O_2$
Sarcine	$C_5H_4N_4O$
Guanine	$C_5H_5N_5O$

These three compounds occur in the animal organism. Xanthine and sarcine have also been obtained by reducing uric acid with sodium amalgam and water, and xanthine is produced by the action of nitrous acid upon guanine.

Xanthine is present in minute quantity in urine, and in nearly all parts of the animal organism; in larger quantity it has been found as a constituent of certain urinary calculi. After the continued use of sulphur-baths urine contains larger quantities of xanthine. It is most conveniently prepared from guanine. Potassium nitrite is added to a solution of guanine in nitric acid, until copious red fumes are evolved. On adding water to the solution a precipitate consisting of xanthine and nitroxanthine is formed, which latter compound is converted into xanthine by reducing it with a ferrous salt.

Xanthine is a white amorphous powder, and sparingly soluble in water. It combines with acids, forming crystallized salts, and also readily dissolves in alkalis. On adding silver nitrate to its aqueous solution, a white gelatinous precipitate of silver-xanthine $C_5H_2N_4O_2Ag_2 + H_2O$ is obtained. By acting with methyl iodide on this body, it is converted into *dimethyl-xanthine* $C_5H_2(CH_3)_2N_4O_2$, which is isomeric with theobromine.

Xanthine dissolves in fuming nitric acid without evolution of a gas. On evaporating this solution a yellow residue is left behind, which on addition of potash-solution assumes a yellow-red colour, which on evaporation changes into violet.

Sarcine or Hypoxanthine occurs in the flesh of vertebrata, and forms a white crystalline powder which is very sparingly soluble in cold water, and unites with bases and acids. Its solution in nitric acid leaves on evaporation a colourless residue, which is not changed by caustic potash.

Guanine occurs in Peruvian guano, in the excrements of spiders, and the pancreatic juice of mammalia. In the so-called guanine-gout of pigs, it is found deposited in the muscles of these animals. To prepare it, guano is boiled with milk of lime, the solution filtered and precipitated with acetic acid. The precipitate, consisting of guanine and uric acid, is dissolved in hot hydrochloric acid, and the guanine precipitated with ammonia.

Guanine is a colourless crystalline powder, which is insoluble in water, alcohol, ammonia, but soluble in acids and potash-solution. It is a bi-acid base, forming two series of salts.

When guanine is heated with potassium chlorate and hydrochloric acid, it is oxidized to *guanidine* (see page 103), parabanic acid, and carbon dioxide:—

$$C_5H_5N_5O + O_3 + H_2O = CH_5N_3 + C_3H_2N_2O_3 + CO_2$$

With nitric acid and caustic potash it gives the same reactions as xanthine.

Carnine $C_7H_8N_4O_3$.—This weak base has been found in "extractum carnis." It forms small colourless crystals, which are sparingly soluble in cold, but freely in boiling water. By the action of bromine-water or nitric acid it is converted into sarcine. This reaction takes place probably according to the following equation:—

$$C_7H_8N_4O_3 + Br_2 = C_5H_4N_4O + HBr + CH_3Br + CO_2$$

CREATINE AND CREATININE.

Creatine $C_4H_9N_3O_2$ occurs in the flesh of all vertebrata, and also in small quantity in the brain and blood. To prepare it, finely chopped meat is exhausted with cold water, and the solution boiled and filtered. To the filtrate baryta-water is added to precipitate phosphoric acid, and the solution evaporated on a water-bath to a syrupy state. On standing creatine gradually crystallizes out, which is purified by recrystallization.

It crystallizes in brilliant prisms containing one molecule of water, and possessing a slightly bitter taste. It dissolves readily in boiling, but only sparingly in cold water.

Creatine combines with acids, forming crystalline but very unstable salts. When boiled with baryta-water, it is resolved into *sarcosine* and urea, and by the action of mercuric oxide on its aqueous solution oxalic acid and *methylguanidine* $CH_4(CH_3)N_3$ are formed:—

$$C_4H_9N_3O_2 + 2HgO = C_2H_2O_4 + C_2H_7N_3 + Hg_2$$

Creatine has been produced artificially by heating an alcoholic solution of sarcosine and freshly-prepared cyanamide to 100° for some hours, and by adding ammonia to a saturated aqueous solution of these two compounds, and allowing the mixture to stand for some time:—

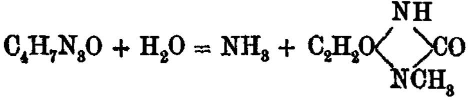
$$C_2H_2O_2N\left\{\begin{matrix} CH_3 \\ H \end{matrix}\right. + NC.NH_2 = C_2H_2O_2N\left\{\begin{matrix} CH_3 \\ C(NH)NH_2 \end{matrix}\right.$$

Creatinine $C_4H_7N_3O$ occurs in urine, and is formed by heating creatine with dilute acids. It can easily be obtained from urine by evaporating it to about one-third of its original bulk, decanting from salt which crystallizes on cooling, and precipitating the liquid with lead acetate, to remove phosphoric acid, &c. The filtrate is freed from lead with sodium carbonate, the solution neutralized with acetic acid, and mercuric chloride is added, which combines with the creatinine, forming a crystalline precipitate.

On decomposing this double salt with hydrogen sulphide a solution of creatinine hydrochloride is obtained, from which the pure salt is prepared by evaporation and recrystallization from alcohol. It forms hard brilliant prisms. On boiling its alcoholic solution with lead oxide the free base is obtained.

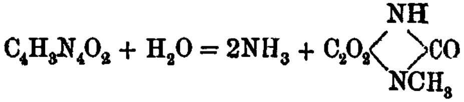
Creatine crystallizes in prisms having a strong alkaline reaction, and being readily soluble in water. With acids it forms crystallizable salts. When dissolved in aqueous alkalis it slowly combines with water, and is converted into creatine. Creatinine combines with several metallic chlorides, as those of mercury, zinc, &c., forming sparingly soluble compounds.

By boiling creatinine with baryta-water it is resolved into ammonia and *methyl-hydantoïn* :—



$$C_4H_7N_3O + H_2O = NH_3 + C_2H_2O\left\langle\begin{matrix}NH\\ NCH_3\end{matrix}\right\rangle CO$$

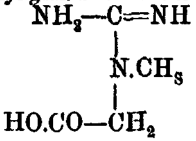
When nitric trioxide is passed into its aqueous solution, a weak basic compound having the composition $C_4H_8N_4O_2$ is formed, which when heated with hydrochloric acid yields ammonia and *methyl-parabanic acid* :—



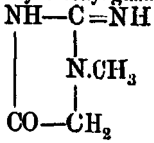
$$C_4H_8N_4O_2 + H_2O = 2NH_3 + C_2O_2\left\langle\begin{matrix}NH\\ NCH_3\end{matrix}\right\rangle CO$$

The synthetical formations of creatine and creatinine, as well as their decompositions, show that the constitution of these compounds is as follows :—

Creatine or
Methyl-guanidine-acetic Acid.



Creatinine or
Glycolyl-methyl-guanidine.



CAFFEINE AND THEOBROMINE.

Theobromine $C_7H_8N_4O_2$.—This weak base occurs in cacao-nuts (from *Theobroma Cacao*), and has also been found in small quantity in the young leaves of Himalaya tea. The nuts are exhausted with hot water; the solution is mixed with basic lead acetate, filtered, and the filtrate treated with hydrogen sulphide to remove the lead, and boiled down to a small bulk, which is exhausted with alcohol to dissolve the theobromine. It is a crystalline powder, sparingly soluble in water, and possessing a slightly bitter taste. When heated with caustic potash it is decomposed with the evolution of methylamine. It combines with acids, forming unstable salts, which are decomposed even by water. It is readily soluble in aqueous ammonia. By adding silver nitrate to this solution a crystalline precipitate of silver theobromine $C_7H_7AgN_4O_2$ is obtained, which when heated with methyl iodide yields *methyl-theobromine* or *caffeine.*

Caffeine, Theine, or Methyl-theobromine $C_8H_{10}N_4O_2$ occurs in the coffee-berries (1 per cent.) and the leaves of the coffee-tree, in tea (2 to 5 per cent.), in the Paraguay-tea (the leaves of *Ilex paraguayensis*), in "guarana" (5 per cent.), a substance resembling cacao, and which is prepared in South America from the fruit of *Paullinia sorbilis*, and also in the kola-nuts, which are used as an article of food in Central Africa. It is prepared from raw coffee-berries or from tea by a process similar to that by which theobromine is obtained from cacao-nuts.

Caffeine crystallizes in long silky needles containing one molecule of water, which escapes on heating. It melts at 234° and sublimes at a higher temperature. It is but sparingly soluble in water, and possesses a faint bitter taste. With acids it forms crystalline salts, which are decomposed by water.

Caffeine acts as a poison when taken in large doses, producing palpitation of the heart and trembling. Cats and rabbits are killed by a dose of 0·4 to 0·5 grams.

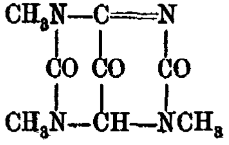
When caffeine is boiled with baryta-water it is resolved into carbon dioxide and *caffeidine* $C_7H_{12}N_4O_2$, a powerful base, which on prolonged boiling with baryta-water is decomposed into carbon dioxide, ammonia, methylamine, formic acid, and sarcosine:—

$$C_7H_{12}N_4O + 5H_2O = CO_2 + NH_3 + 2CH_3.NH_2 + CH_2O_2 + C_3H_7NO_2$$

The action of chlorine upon an aqueous solution of caffeine produces cyanogen chloride, methylamine, and *amalic acid* or *tetramethylalloxantin* $C_8(CH_3)_4N_4O_7 + H_2O$, colourless crystals, which are coloured violet by alkalis, and produce red stains on the skin.

By the further action of chlorine upon this compound *cholestrophane* or *dimethylparabanic acid* is produced, which is also formed by treating silver parabanate with methyl iodide (see page 247).

The products of decomposition of caffeine prove that this body has a constitution similar to those of creatine and uric acid. The following constitution at least readily explains the action of baryta-water upon caffeine:—



$$\begin{array}{ccccc} CH_3N & — & C & = & N \\ | & & | & & | \\ CO & & CO & & CO \\ | & & | & & | \\ CH_3N & — & CH & — & NCH_3 \end{array}$$

COMPOUNDS OF TRIAD RADICALS.

We are as yet only acquainted with one alcohol of a triad radical, viz. *glycerin* or propenyl alcohol. The derivatives of this compound, which have been very completely investigated, are much more numerous and varied than those of monad and dyad radicals, as the following table will show:—

PROPENYL ALCOHOL OR GLYCERIN $\mathrm{C_3H_5}\left\{\begin{matrix}\mathrm{OH}\\ \mathrm{OH.}\\ \mathrm{OH}\end{matrix}\right.$

Monochlorhydrin.

$$\mathrm{C_3H_5}\left\{\begin{matrix}\mathrm{Cl}\\ \mathrm{OH}\\ \mathrm{OH}\end{matrix}\right.$$

Dichlorhydrin.

$$\mathrm{C_3H_5}\left\{\begin{matrix}\mathrm{Cl}\\ \mathrm{Cl}\\ \mathrm{OH}\end{matrix}\right.$$

Trichlorhydrin or Propenyl Trichloride.

$$\mathrm{C_3H_5}\left\{\begin{matrix}\mathrm{Cl}\\ \mathrm{Cl}\\ \mathrm{Cl}\end{matrix}\right.$$

Trinitrin or Propenyl Trinitrate.

$$\mathrm{C_3H_5}\left\{\begin{matrix}\mathrm{NO_3}\\ \mathrm{NO_3}\\ \mathrm{NO_3}\end{matrix}\right.$$

Chlorodinitrin.

$$\mathrm{C_3H_5}\left\{\begin{matrix}\mathrm{Cl}\\ \mathrm{NO_3}\\ \mathrm{NO_3}\end{matrix}\right.$$

Dichloronitrin.

$$\mathrm{C_3H_5}\left\{\begin{matrix}\mathrm{Cl}\\ \mathrm{Cl}\\ \mathrm{NO_3}\end{matrix}\right.$$

Monethylin.

$$\mathrm{C_3H_5}\left\{\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\\ \mathrm{OC_2H_5}\end{matrix}\right.$$

Diethylin.

$$\mathrm{C_3H_5}\left\{\begin{matrix}\mathrm{OH}\\ \mathrm{OC_2H_5}\\ \mathrm{OC_2H_5}\end{matrix}\right.$$

Triethylin or Propenyl-triethyl Ether.

$$\mathrm{C_3H_5}\left\{\begin{matrix}\mathrm{OC_2H_5}\\ \mathrm{OC_2H_5}\\ \mathrm{OC_2H_5}\end{matrix}\right.$$

Monacetin.

$$\mathrm{C_3H_5}\left\{\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\\ \mathrm{OC_2H_3O}\end{matrix}\right.$$

Diacetin.

$$\mathrm{C_3H_5}\left\{\begin{matrix}\mathrm{OH}\\ \mathrm{OC_2H_3O}\\ \mathrm{OC_2H_3O}\end{matrix}\right.$$

Triacetin.

$$\mathrm{C_3H_5}\left\{\begin{matrix}\mathrm{OC_2H_3O}\\ \mathrm{OC_2H_3O}\\ \mathrm{OC_2H_3O}\end{matrix}\right.$$

Succinin.

$$\mathrm{C_3H_5}\left\{\begin{matrix}\mathrm{OH}\\ \left.\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}\right\}\mathrm{C_4H_4O_2}\end{matrix}\right.$$

Glycerin-sulphuric Acid.

$$\mathrm{C_3H_5}\left\{\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\\ \mathrm{SO_4H}\end{matrix}\right.$$

Glycerin-phosphoric Acid.

$$\mathrm{C_3H_5}\left\{\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\\ \mathrm{PO_4H_2}\end{matrix}\right.$$

The propenyl compounds are intimately connected with propyl and propene compounds; they are derivatives of propane:—

Propane.

$$\begin{array}{c}\mathrm{CH_3}\\ |\\ \mathrm{CH_2}\\ |\\ \mathrm{CH_3}\end{array}$$

Propyl Alcohol.

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

Propene Alcohol.

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

Propenyl Alcohol.

$$\begin{array}{c}\mathrm{CH_2.OH}\\ |\\ \mathrm{CH_2.OH}\\ |\\ \mathrm{CH_2.OH}\end{array}$$

Most fats and oils are mixtures of propenyl ethers of the fatty acids $C_nH_{2n}O_2$ and the acids of the oleic series $C_nH_{2n-2}O_2$. Glycerin has also been found in small quantities amongst the products of vinous fermentation, and is present in wine and beer.

When fats are heated with water or with alkalis they are converted into glycerin and acids or their alkali-salts (*soaps*).[1]

---

[1] This process is called *saponification*. This term was originally restricted to this decomposition of fats by alkalis, but it is now generally applied to the decomposition of compound ethers into acids and alcohols.

Glycerin was first obtained by heating olive oil, water, and lead oxide; insoluble lead salts are thereby formed (*lead plaster*), while glycerin remains in solution. The latter is freed from lead by hydrogen sulphide, and the solution evaporated. Glycerin is now obtained in large quantities and in a state of great purity in the manufacture of stearin candles. The fats, as tallow, &c., are distilled by means of overheated steam; the distillate separates into two layers, the lower one consisting of an aqueous solution of glycerin, while the upper one contains the acids. The solution of glycerin is concentrated by evaporation, and the residue again distilled with steam in an apparatus in which glycerin condenses, whilst the much more volatile steam escapes.

Glycerin can also be produced artificially from *propane*. By the action of chlorine on this compound a large quantity of propene dichloride is formed, which, when heated with iodine chloride, is converted into propenyl trichloride $C_3H_5Cl_3$. This chloride is decomposed by heating with water to 170°, the products being hydrochloric acid and glycerin.

Pure glycerin is a colourless, very viscid liquid, having a specific gravity of 1·27. It can be mixed with water and alcohol in all proportions, and possesses a very sweet taste. When exposed to strong winter-cold it sometimes solidifies to transparent and strongly refractive hard crystals; but commonly it remains liquid, and solidifies only at —40° to an amorphous gum-like mass. When quickly heated it distils at 280°, with partial decomposition; but under a diminished pressure it may be distilled without alteration, boiling at 210° under a pressure of 50 mm.

When glycerin is added to an alcoholic solution of sodium ethylate, the compound $C_3H_5\begin{cases}OH\\OH + C_2H_5.OH\\ONa\end{cases}$ separates out in small crystals grouped in stars, which at 100° lose alcohol, a white deliquescent powder of *monosodium glycerate* being left behind.

When yeast is added to an aqueous solution of glycerin, and the mixture is allowed to stand at a temperature of 20° to 30° for some months, propionic acid is produced.

Glycerin is easily reduced to secondary propyl iodide by distilling it with an excess of concentrated hydriodic acid:—

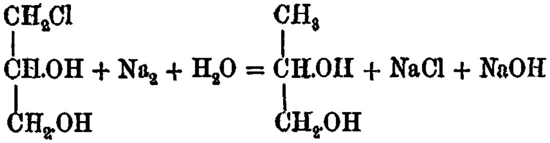
$$C_3H_8O_3 + 5HI = C_3H_7I + 3H_2O + 2I_2$$

Secondary propyl-iodide is generally obtained by this method; in preparing it amorphous phosphorus is added to the mixture, which converts the free iodine again into hydriodic acid:—

$$C_3H_8O_3 + H_2O + P + I = C_3H_7I + H_3PO_4$$

Monochlorhydrin or Propenyl Monochlorhydrate $C_2H_5Cl(OH)_2$ is obtained by saturating glycerin with hydrochloric acid gas and heating the mixture for some time to 100°.

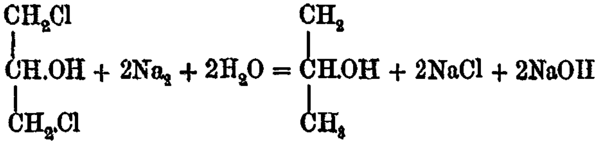
It is a liquid having an ethereal smell, and boiling at 225° to 230°. By acting with sodium amalgam on its aqueous solution it is reduced to propene glycol:—



$$\begin{array}{l} CH_2Cl \\ | \\ CH.OH + Na_2 + H_2O = \\ | \\ CH_2.OH \end{array} \begin{array}{l} CH_3 \\ | \\ CH.OH + NaCl + NaOH \\ | \\ CH_2.OH \end{array}$$

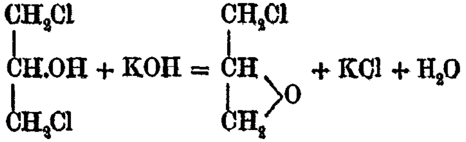
When chlorhydrin is heated with trimethylamine, *trimethylglycerammonium chloride* $N(CH_3)_3C_3H_5(OH)_2Cl$ is obtained in white needles, which are readily soluble in water. The free base, which has a constitution similar to that of choline (page 190), has not yet been prepared.

Dichlorhydrin or Propenyl Dichlorhydrate $C_3H_5Cl_2(OH)$.—This body is produced when glycerin is heated with a large excess of fuming hydrochloric acid, and by the action of phosphorus pentachloride upon glycerin, but is most conveniently prepared by saturating a mixture of glycerin and glacial acetic acid with hydrochloric acid at 100°. It is an oily liquid, possessing an agreeable smell, and boiling at 178°. By the action of water and sodium amalgam it is reduced to dimethyl carbinol:—



$$\begin{array}{l} CH_2Cl \\ | \\ CH.OH + 2Na_2 + 2H_2O = \\ | \\ CH_2.Cl \end{array} \begin{array}{l} CH_2 \\ | \\ CH.OH + 2NaCl + 2NaOH \\ | \\ CH_3 \end{array}$$

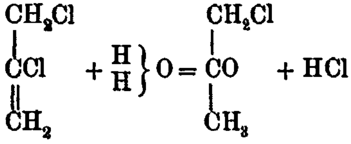
By heating it with potash solution, hydrochloric acid is taken out, and *epichlorhydrin* or *monochloropropene oxide* C_3H_5ClO produced:—



$$\begin{array}{l} CH_2Cl \\ | \\ CH.OH + KOH = \\ | \\ CH_2Cl \end{array} \begin{array}{l} CH_2Cl \\ | \\ CH \diagdown \\ \mid \quad \rangle O \\ CH_2 \diagup \end{array} + KCl + H_2O$$

Epichlorhydrin boils at 119°; it smells like chloroform, and has a burning sweet taste. It combines with acids like propene oxide; with hydrochloric acid it forms again dichlorhydrin, and on heating it with acetic acid it yields *acetochlorhydrin* $C_3H_5\left\{\begin{array}{l} Cl \\ O.C_2H_3O \\ OH \end{array}\right.$; it also unites with water, monochlorhydrin or monochloropropene glycol being thereby formed.

Trichlorhydrin or Propenyl Trichloride $C_3H_5Cl_3$.—This compound is produced by the action of phosphorus pentachloride upon glycerin or the chlorhydrins, and together with an isomeric compound when propene dichloride is heated with iodine chloride to 170°. It is a colourless liquid, possessing a smell like chloroform, and boiling at 158°. On heating it with caustic alkalis a violent reaction sets in, and *dichloroglycide* distils over, a heavy liquid possessing a garlic-like smell, and boiling at 98°. It combines readily with one molecule of chlorine and bromine, and dissolves in concentrated sulphuric acid with the evolution of hydrochloric acid. On distilling this solution with a large quantity of water, it yields monochloracetone :—



$$\begin{matrix} CH_2Cl \\ | \\ CCl \\ \| \\ CH_2 \end{matrix} + \left.\begin{matrix} H \\ H \end{matrix}\right\} O = \begin{matrix} CH_2Cl \\ | \\ CO \\ | \\ CH_3 \end{matrix} + HCl$$

Bromhydrins.—These compounds are produced by the action of hydrobromic acid or phosphorus pentabromide upon glycerin.

Tribromhydrine or Propenyl Tribromide $C_3H_5Br_3$ is a thick, colourless liquid, boiling at 220°, and solidifying at a low temperature to large brilliant prisms, melting at 16°. On heating it with an alcoholic solution of potassium cyanide, it yields *propenyl tricyanide* or the nitrite of tricarballylic acid $C_3H_5(CN)_3$ (see page 238).

Sulphydrins are formed by treating the different chlorhydrins with an alcoholic solution of potassium hydrosulphide. *Monosulphydrin* $C_3H_5\left\{\begin{matrix} OH \\ OH \\ SH \end{matrix}\right.$ is a viscid non-volatile liquid, possessing a very disagreeable odour. The hydrogen in the group SH can easily be replaced by metals, just as in other mercaptans. *Disulphydrin* $C_3H_5\left\{\begin{matrix} OH \\ SH \\ SH \end{matrix}\right.$ and *Trisulphydrin* $C_3H_5\left\{\begin{matrix} SH \\ SH \\ SH \end{matrix}\right.$ have similar properties.

Glycerinsulphuric Acid $C_3H_5\left\{\begin{matrix} OH \\ OH. \\ O.SO_3H \end{matrix}\right.$ —This monobasic acid is formed by mixing glycerin with concentrated sulphuric acid. It forms soluble salts with barium and calcium. By decomposing their solution with sulphuric acid or with oxalic acid, an aqueous solution of glycerinsulphuric acid is obtained, which has a very sour taste. On evaporation it is resolved into glycerin and sulphuric acid.

Glycerinphosphoric Acid $C_3H_5\left\{\begin{matrix} OH \\ OH. \\ O.PO(OH)_2 \end{matrix}\right.$ —Glacial phosphoric acid dissolves in glycerin with the evolution of heat. On diluting with water and neutralizing with barium carbonate a solution of *barium glycerinphosphate* is obtained, which is decomposed by sulphuric acid. On evaporating the solution *in vacuo*, glycerinphosphoric acid is obtained as a strongly sour thick liquid, which decomposes on heating. It is a bibasic acid, forming crystallized salts.

Trinitrin, or Propenyl Nitrate $C_3H_5(NO_3)_3$.—This body, commonly called "nitroglycerin," is obtained by dissolving glycerin in a well-cooled mixture of concentrated sulphuric acid and saltpetre. On pouring the solution in cold water, nitroglycerin separates out. It is a heavy, colourless, oily liquid, possessing a burning sweet taste and poisonous properties, the inhalation of the vapour producing severe headache. It is a very dangerous compound, exploding on heating it or by percussion with the utmost violence. It has been much employed for blasting in mines and quarries, but it is very dangerous to handle, and has given rise to many fatal accidents. It is therefore now not used in the pure state, but mixed with finely divided silica (so-called "kieselguhr," the remains of infusoria): this mixture, known by the name of "dynamite," is much less dangerous than the pure substance.

By dissolving monochlorhydrin in a mixture of nitric acid and sulphuric acid, *monochlordinitrin* $C_3H_5\left\{\begin{matrix}Cl\\NO_3\\NO_3\end{matrix}\right.$ is obtained, an oily liquid which does not explode by percussion, but is highly inflammable. The same compound is produced by the action of nitric acid upon epichlorhydrin.

A very similar compound is *dichlormononitrin* $C_3H_5\left\{\begin{matrix}Cl\\NO_3\\NO_3\end{matrix}\right.$, which has been obtained by the same reaction from dichlorhydrin.

Ethyl-ethers of Propenyl.—These ethers are produced by the action of sodium ethylate upon monochlorhydrine and dichlorhydrine.

Ethylhydrin $C_3H_5\left\{\begin{matrix}OC_2H_5\\(OH)_2\end{matrix}\right.$ boils at 230°, and *diethylhydrin* $C_3H_5\left\{\begin{matrix}(OC_2H_5)_2\\OH\end{matrix}\right.$ is a liquid possessing an aromatic smell, and boiling at 191°.

Triethylhydrin $(C_3H_5OC_2H_5)_3$, a liquid boiling at 185°, is formed by dissolving sodium in diethylhydrin and treating the product with ethyl iodide.

PROPENYL-ETHERS OF THE FATTY ACIDS.

By heating glycerin with fatty acids, compound propenyl ethers are formed, the three atoms of hydrogen in the hydroxyl-groups being replaced, one after the other, by the acid radical. Most of the different fats and oils consist of mixtures of such ethers, each containing three acid radicals.

Monoformin $C_3H_5\left\{\begin{matrix}(OH)_2\\ O,COH\end{matrix}\right.$ is formed by heating glycerin with oxalic acid. It is an oily liquid, soluble in water. On heating this solution, monoformin is resolved into glycerin and formic acid.

Monacetin $C_3H_5\left\{\begin{matrix}(OH)_2\\ OC_2H_3O\end{matrix}\right.$, an oily liquid, which is soluble in water and possesses an ethereal smell, is formed by heating glycerin with acetic acid to 100°; while by heating the mixture to 200°, *diacetin* $C_3H_5\left\{\begin{matrix}OH\\ (OC_2H_3O)_2\end{matrix}\right.$ is obtained, an oily liquid boiling at 280°. When this body is heated with a very large excess of acetic acid to 250°, it is converted into *triacetin* $C_3H_5(OC_2H_3O)_3$, a liquid which is insoluble in water and boils at 286°. This compound exists in the oil contained in the seeds of the common spindle-tree (*Euonymus europæus*), and has also been produced by heating propenyl tribromide with silver acetate.

The three *butyrins* are oily neutral liquids; tributyrin is found in butter, together with *tricapronin*, *tricaprylin*, and *tricaprin*; *trimyristin* occurs in nutmeg-butter.

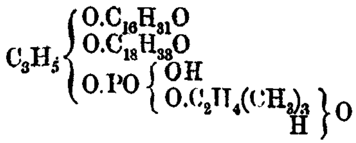
Monopalmitin melts at 49°, dipalmitin at 59°; both compounds are produced by heating glycerin with palmitic acid in sealed tubes. By using a large excess of palmitic acid and heating the mixture to 250° for twenty-four hours, *tripalmitin* is formed, a compound occurring in many fats. It is prepared by exposing olive oil to a strong cold, and subjecting the solid mass to a strong pressure to remove liquid triolein. Tripalmitin crystallizes from alcohol in pearly scales, melting at 61°.

Tristearin occurs in almost all solid fats, and may be extracted from beef or mutton suet by means of ether. After being purified by repeated crystallizations, it is obtained in pearly crystals melting at 66°·5 and solidifying to an amorphous mass.

Lecithine $C_{42}H_{84}NPO_9$.—This complicated derivative of glycerin-phosphoric acid is found widely distributed in the animal organism, occurring in the brain, in the nerves, in the yolk of eggs, in the blood-corpuscles, &c. It is most conveniently prepared by exhausting the yolk of eggs with a mixture of alcohol and ether. The solution is gently heated until all the ether has volatilized, and alcohol added to the residue, by which fats are precipitated. The solution is filtered and platinum tetrachloride is added; a yellow precipitate having the composition $2(C_{42}H_{83}NPO_8Cl) + PtCl_4$ is formed, which is decomposed by hydrogen sulphide. The lecithine hydrochloride thus obtained is dissolved in a mixture of alcohol and ether, and the solution shaken with silver oxide, and, after filtration, again treated with hydrogen sulphide in order to precipitate silver which has gone in solution.

Pure lecithine is a wax-like, indistinctly crystalline mass, soluble in alcohol and ether; in water it softens and becomes gelatinous, but does not dissolve. It combines not only with acids, but also forms metallic compounds, and very readily undergoes decomposition by boiling its alcoholic solution alone, or quicker in presence of alkalis or acids, the products being *choline*, *glycerin-phosphoric acid*, and *fatty acids* (palmitic acid and oleïc acid $C_{18}H_{34}O_2$).

This decomposition, together with the chemical character of lecithine, explain its constitution:—



$$C_3H_5\begin{cases}O.C_{16}H_{31}O\\ O.C_{18}H_{33}O\\ O.PO\begin{cases}OH\\ \left.\begin{matrix}O.C_2H_4(CH_3)_3\\ H\end{matrix}\right\}O\end{cases}\end{cases}$$

Lecithine is glycerin-phosphoric acid in which two atoms of hydrogen in the hydroxyl-groups of glycerin are replaced by the radicals of oleïc and palmitic acids, whilst cholin, a compound being at the same time an ammonium-base and an alcohol, forms with glycerin-phosphoric acid an acid compound ether. Lecithine is therefore at the same time a fat, a base, and an acid.

It appears very probable that several lecithines exist, containing radicals of different fatty acids.

GLYCERIC ACID $C_3H_6O_4$.

To prepare this acid, glycerine is diluted with an equal volume of water and poured on the top of strong nitric acid contained in a high cylinder. The mixture, after standing for several days, is evaporated on a water-bath, and the syrupy residue dissolved in water and neutralized with lead oxide. The lead glycerate is purified by recrystallization, and an aqueous solution of the pure salt decomposed by hydrogen sulphide.

On evaporating the filtrate on a water-bath, glyceric acid remains behind as a thick, syrupy, and very sour liquid.

On heating it is resolved into water and pyruvic acid (see page 230); when it is fused with caustic potash it is resolved into acetic acid and formic acid.

By the action of phosphorus iodide and water it is reduced to β iodopropionic acid.

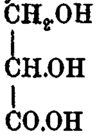
β Iodopropionic Acid $C_3H_5IO_2$ forms white pearly crystals melting at 82°. When its aqueous solution is heated with silver oxide, *hydracrylic acid* $C_3H_5(OH)O_2$ is formed, a compound which is isomeric with the lactic acids, and forms like them a sour, syrupy liquid, but differs from them by not yielding lactide on heating, but by being resolved into *acrylic* $C_3H_4O_2$ and water.

Phosphorus pentachloride converts glyceric acid into *β chloropropionyl chloride,* which is readily acted upon by water, being converted into *β chloropropionic acid*, which forms fibrous crystals smelling like creosote and melting at 65°.

Amidoglyceric Acid or Serine ($C_3H_4O_3NH_2$).—This compound has been obtained by boiling sericin or silk-gelatin (see Silk) with dilute sulphuric acid. It crystallizes from a hot solution in hard brittle crystals, and forms metallic salts, but combines also with acids. By the action of nitrous acid it is converted into glyceric acid.

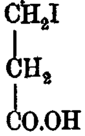
The constitution of glyceric acid and its derivatives is generally represented by the following formulæ:—

Glyceric Acid.



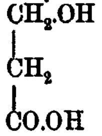
$$\begin{array}{l} CH_2.OH \\ | \\ CH.OH \\ | \\ CO.OH \end{array}$$

β Iodopropionic Acid.



$$\begin{array}{l} CH_2I \\ | \\ CH_2 \\ | \\ CO.OH \end{array}$$

Hydracrylic Acid.

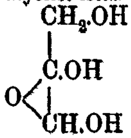


$$\begin{array}{l} CH_2.OH \\ | \\ CH_2 \\ | \\ CO.OH \end{array}$$

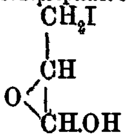
If hydracrylic acid had this constitution it would be identical with ethene-lactic acid, which on oxidation is converted into malonic acid. But hydracrylic acid does not yield a trace of this compound, but is resolved into carbon dioxide, glycollic acid, and oxalic acid, and no acetic acid is formed, showing that hydracrylic acid does not contain the group methyl, and therefore its constitution is also quite different from that of common lactic acid.

When an alcohol is oxidized, the oxygen entering the molecule is attracted by that carbon atom which is already combined with oxygen. Now in glycerin each of the three carbon atoms is combined with oxygen, and consequently the oxygen which replaces the hydrogen will be attracted as much by the second carbon atom as by the first. From this it appears very probable that the above compounds have the following constitution:—

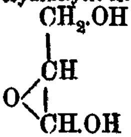
Glyceric Acid.



β Iodopropionic Acid.



Hydracrylic Acid.



Compounds having such a constitution would be acids, for organic hydroxides are converted into acids, not only by the transformation of *methoxyl* $CH_2.OH$ into *carboxyl* $CO.OH$, but always when negative elements or radicals (O, Cl, NO_2) accumulate near an alcoholic hydroxyl.

ALLYL-COMPOUNDS.

These compounds contain the radical *allyl* C_3H_5, which differs from propenyl by being a monad radical, two of the carbon atoms being linked together by two of the combining units of each. The name of this radical is derived from the fact that some of its compounds occur in *Allium-species* (garlic, &c.). The allyl-compounds combine with hydrogen, chlorine, &c., yielding thus either propyl- or propenyl compounds.

Allyl Alcohol $C_3H_5.OH$.—When a mixture of glycerin and crystallized oxalic acid is heated, carbon dioxide is evolved, and at about 100° dilute formic acid begins to distil over; by raising the temperature the evolution of carbon dioxide ceases, but begins again at 190°, and a mixture of allyl alcohol and other products distils. Monoformin is formed, which at a lower temperature is acted upon by water, yielding formic acid and glycerine, whilst at a higher temperature it is resolved into allyl alcohol, carbon dioxide, and water :—

$$C_3H_5\left\{\begin{array}{l}OH\\ OH\\ O.COH\end{array}\right. = C_3H_5.OH + CO_2 + H_2O$$

To obtain pure allyl alcohol the product is treated with caustic potash, distilled again, and rectified over anhydrous baryta. It is a limpid liquid, boiling at 97°, and possessing a characteristic pungent smell (like most allyl-compounds).

When allyl alcohol is oxidized with dilute chromic acids, it yields formic acid, but no acetic acid, showing that it does not contain the group CH_3, but has the constitution $CH_2{=}CH{-}CH_2.OH$.

Allyl alcohol does not combine readily with hydrogen; it is not changed by acting with sodium amalgam or zinc and hydrochloric acid on its aqueous solution. But when it is heated with an equal weight of caustic potash in a flask connected with a reversed condenser, an evolution of hydrogen commences at 105°, and goes on up to 155°. On distilling the solid mass thus obtained with water, a mixture of ethyl alcohol and propyl alcohol (about 20 per cent. of the allyl alcohol employed) is obtained, and the residue contains potassium formate, and salts of other acids.

Allyl alcohol readily combines with chlorine, forming dichloropropyl alcohol, a liquid boiling at 182°, which is isomeric with dichlorhydrin:—

$$\begin{array}{ccc}\text{Dichlorhydrin.} & \qquad & \text{Dichloropropyl Alcohol.}\\ CH_2Cl & & CH_2Cl\\ | & & |\\ CH.OH & & CHCl\\ | & & |\\ CH_2.Cl & & CH_2.OH\end{array}$$

Dibromopropyl Alcohol $C_3H_5Br_2.OH$ boils at 219°; by the action of nascent hydrogen it yields propyl alcohol, and on heating it with caustic potash, glycerin is produced.

Monobromallyl Alcohol $C_3H_4Br.OH$.—When propenyl tribromide is distilled with caustic potash, it is acted upon analogous to propenyl trichloride (page 256), *dibromoglycide* $CH_2Br—CBr═CH_2$ being formed. By heating this body with an alcoholic solution of potassium acetate it is converted into *monobromallyl acetate*, a liquid having a refreshing smell and boiling at 164°. This ether is decomposed by caustic alkalis, *monobromallyl alcohol* $HO.CH_2—CBr═CH_2$ being produced, a mobile limpid liquid boiling at 155°, and possessing a pleasant refreshing odour. Phosphorus pentachloride converts it into *monobromallyl chloride* C_3H_4BrCl, a colourless heavy liquid boiling at 120°.

Allyl Chloride C_3H_5Cl is a limpid liquid, boiling at 45°, which has been prepared by heating allyl iodide with mercuric chloride and spirits of wine. It combines with chlorine to propenyl trichloride.

Allyl Bromide $C_{53}H_5Br$ is obtained by the action of phosphorus bromide on allyl alcohol; it boils at 70°, and combines with bromine to propenyl tribromide.

Allyl Iodide C_3H_5I may be produced by acting with iodine and phosphorus upon allyl alcohol; but is more conveniently prepared from glycerin. Six parts of iodine are placed into a retort, ten parts of anhydrous glycerin poured on it, and three parts of phosphorus are added. A violent reaction soon sets in, the mixture taking fire, and allyl iodide distils; towards the end heat must be applied to drive the whole of the iodide over:—

$$C_3H_5(OH)_3 + P + I = C_3H_5I + PO_3H_3$$

On passing hydriodic acid gas into allyl iodide, the liquid becomes hot, free iodine separates out, and isopropyl iodide is formed. In the preparation of the latter compound from glycerin and hydriodic acid, first allyl iodide is formed, which by an excess of hydriodic acid is further acted upon. If this acid be not present in excess, the product consists of a mixture of allyl iodide and isopropyl iodide:—

$$(1)\quad C_3H_5(OH)_3 + 3HI = C_3H_5I + 3H_2O + I_2$$

$$(2)\quad C_3H_5I + 2HI = C_3H_7I + I_2$$

By the action of chlorine upon allyl iodide, *propenyl trichloride* is produced, whilst bromine converts it into *propenyl tribromide*.

When an alcoholic solution of allyl iodide is shaken with mercury, *mercury-allyl iodide* C_3H_5HgI is formed, which crystallizes from an alcoholic solution in shining scales. On heating with iodine it is again converted into allyl iodide, whilst when heated by itself it yields mercurous iodide and *diallyl* C_6H_{10}, a hydrocarbon which is also formed by the action of sodium upon allyl iodide.

Allyl iodide is used for the preparation of pure propene. To prepare it, either mercury-allyl iodide is treated with hydrochloric acid, or allyl iodide is acted upon by zinc and hydrochloric acid.

Diallyl Ether or Allyl Oxide $\left.\begin{matrix}C_3H_5\\C_3H_5\end{matrix}\right\}O$.—Small quantities of this compound occur in the essential oil of garlic. It is easily produced by dissolving sodium in allyl alcohol, and acting upon the sodium allylate with allyl iodide, or by heating the latter compound with silver oxide. Diallyl ether is a limpid, mobile liquid, boiling at 82°, and possessing a pungent smell.

Ethyl-allyl Ether $\left.\begin{matrix}C_2H_5\\C_3H_5\end{matrix}\right\}O$ is formed by heating sodium ethylate with allyl iodide; it boils at 62°, and easily combines with a molecule of chlorine and bromine. The dichloride thus obtained is the ethyl-ether of dichlorhydrin. On distilling it over caustic soda it loses one molecule of hydrochloric acid, and yields *ethyl-monochlorallyl ether* $\left.\begin{matrix}C_2H_5\\C_3H_4Cl\end{matrix}\right\}O$, a liquid boiling at 120°. The dibromhydrin-ethyl ether is acted upon by alkalis in a similar way, being converted into *ethyl-monobromallyl ether* $\left.\begin{matrix}C_2H_5\\C_3H_4Br\end{matrix}\right\}O$, a limpid liquid, possessing a pleasant odour and boiling at 135°.

Allyl Hydrosulphide or Allyl Mercaptan $\left.\begin{matrix}C_3H_5\\H\end{matrix}\right\}S$ is a liquid boiling at 90°, smelling like ethyl mercaptan, and forming, like the latter, metallic compounds. It is produced by the action of allyl iodide upon potassium hydrosulphide.

Allyl Sulphide $\left.\begin{matrix}C_3H_5\\C_3H_5\end{matrix}\right\}S$ is the principal constituent of the volatile oil of garlic, and has been produced artificially by distilling allyl iodide with an alcoholic solution of potassium sulphide. It is a colourless liquid of high refractive power, boiling at 140° and possessing the peculiar odour of garlic in the highest degree. On mixing it with an alcoholic solution of silver nitrate, a crystalline precipitate $(C_3H_5)_2S + 2AgNO_3$ is formed, which is decomposed by aqueous ammonia, the products being ammonium nitrate, silver sulphide, and allyl oxide.

Allyl sulphide occurs also in other Allium species, and probably in the volatile oil of *asafœtida*.

Allyl Cyanides.—When silver cyanide is acted upon by allyl iodide, *allyl carbamine* $CN.C_3H_5$ is formed, a liquid possessing a most overwhelming nauseous odour. It is isomeric with *crotonitrile* $NC.C_3H_5$, a liquid occurring in small quantity in the essential oil of mustard. This nitrile is also produced by heating potassium cyanide with allyl iodide. It is a limpid liquid, possessing the odour of leek, and boiling at 118°.

Allyl Sulphocarbimide or Oil of Mustard $\left.\begin{matrix}C_3H_5\\CS\end{matrix}\right\}N$.—The seeds of black mustard contain a peculiar compound called *myronic acid* (see Glucosides), which in contact with water and a ferment contained in the seeds is resolved into acid potassium sulphate, sugar, and oil of mustard. To prepare mustard-oil, the seeds are crushed and pressed to remove the fatty oil, and the residue is mixed with water and distilled. It can also be obtained by heating allyl iodide with potassium sulphocyanate. In this reaction allyl sulphocyanate (a compound not yet known) is probably first formed, but undergoes a molecular change at the high temperature at which the reaction takes place. Oil of mustard is a transparent, strongly refractive liquid, boiling at 148°, and possessing in the highest degree the sharp pungent odour of mustard. It rapidly blisters the skin, and its vapour excites tears, and produces even in a small quantity inflammation of the eyes. On repeated distillation with water it resolves into sulphur and crotonitrile. Nascent hydrogen converts it into allylamine and *metasulphoformaldehyde* $(C_2H_2S)_3$:—

$$N\left\{\begin{matrix}C_3H_5\\CS\end{matrix}\right. + 2H_2O = N\left\{\begin{matrix}C_3H_5\\H_2\end{matrix}\right. + C_2H_2S$$

Monochlorallyl Sulphocarbimide $\left.\begin{matrix}C_3H_4Cl\\CS\end{matrix}\right\}N$ is obtained by the action of potassium sulphocyanate upon *dichloroglycide* (monochlorallyl chloride, see page 256). It is a liquid boiling at 185°, and possessing a very sharp penetrating smell.

Amines of Allyl.—These bases are formed by heating allyl iodide with ammonia; the principal product of the reaction consisting of *tetrallylammonium iodide* $N(C_3H_5)_4I$, a crystalline salt which when treated in aqueous solution with silver oxide is converted into the corresponding hydroxide, a strongly alkaline and caustic body.

Allylamine $C_3H_5.NH_2$ is conveniently prepared by the action of zinc and hydrochloric acid upon an alcoholic solution of oil of mustard, and subsequent distillation with caustic potash. It is a limpid liquid possessing an ammoniacal smell and boiling at 58°.

Dimonochlorallylamine $\left.\begin{matrix}C_3H_4Cl\\C_3H_4Cl\\H\end{matrix}\right\}N$ is formed by the action of ammonia upon a solution of trichlorhydrin in alcohol. It is a heavy oily liquid, boiling at 190°, possessing an ammoniacal smell, and combining with acids forming deliquescent salts.

Thiosinnamine or Allyl Sulphocarbamide $CS\left\{\begin{matrix}NH_2\\NH.C_3H_5\end{matrix}\right.$ is formed by the direct combination of ammonia and oil of mustard. It crystallizes in brilliant colourless prisms, soluble in water, and possessing a bitter taste. With acids it forms salts, which have an acid reaction and are decomposed by water. On heating with water and lead oxide it is decomposed with the production of lead sulphide and *sinnamine* or *allyl cyanamide* $N\left\{\begin{matrix}C_3H_5\\CN,\\H\end{matrix}\right.$ a powerful base, which is soluble in water and possesses a very bitter taste.

Diallyl Carbamide or Sinapoline $CO\left\{\begin{matrix}NH.C_3H_5\\NH.C_3H_5\end{matrix}\right.$ is produced, together with carbon dioxide and lead sulphide, by heating oil of mustard with water and lead oxide:—

$$N\left\{\begin{matrix}C_3H_5\\CS\end{matrix}\right. + 2PbO + H_2O = CO\left\{\begin{matrix}NH.C_3H_5\\NH.C_3H_5\end{matrix}\right. + PbS_2 + CO_2$$

It is soluble in water and crystallizes in shining scales, having an alkaline reaction.

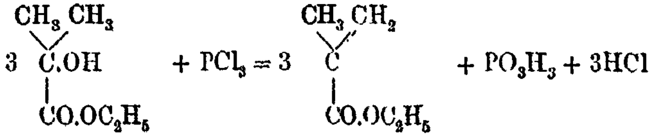
ACIDS OF THE SERIES $C_nH_{2n-2}O_2$.

Allyl alcohol is a primary alcohol; on oxidation it yields *acraldehyde* C_3H_4O and *acrylic acid* $C_3H_4O_2$. Acrylic acid is the first member of a homologous series of acids, of which the corresponding alcohols are not known. The following table contains the acids of this group which are best studied:—

Acrylic Acid . .	$C_3H_4O_2$	Cimicic Acid .	$C_{14}H_{26}O_2$
Crotonic „ . .	$C_4H_6O_2$	Hypogæic „ .	$C_{16}H_{30}O_2$
Angelic „ . .	$C_5H_8O_2$	Oleic „ .	$C_{18}H_{34}O_2$
Pyroterebic Acid.	$C_6H_{10}O_2$	Erucic „ .	$C_{22}H_{42}O_2$

Some of these acids exist as glycerides in fats, and others have been prepared artificially by different reactions. A series of acids which are isomeric with those contained in the table have been obtained from oxalic acid. By acting on ethyl oxalate with the zinc compounds of alcohol radicals we obtain ethyl-ethers of the so-called isolactic acids, and by treating the latter with phosphorus trichloride they lose water and are converted into ethers of the acids of the *iso-acrylic series.*

Thus the ethyl-ether of oxy-isobutyric or dimethyloxalic acid yields the ethyl-ether of methacrylic acid, which is isomeric with crotonic acid:—

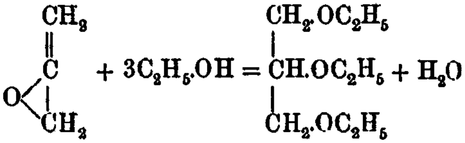


A very characteristic reaction of the acids of this group is that when they are fused with caustic potash they are resolved into two fatty acids. This decomposition gives the clue to their constitution, as always those two carbon atoms are torn asunder which are linked together by two of the combining units of each.

Acrylaldehyde or Acrolein C_3H_4O is easily obtained by depriving glycerin of the elements of water :—

$$C_3H_8O_3 - 2H_2O = C_3H_4O$$

This is best effected by heating glycerin with acid potassium sulphate or phosphorus pentoxide. It is a colourless liquid boiling at 52°·4. Its vapour is most irritating, attacking most violently the mucous membranes of the nose and eyes. It is the cause of the intolerable odour given off by fats and glycerin when subjected to destructive distillation. It is a very unstable body; in closed vessels it soon changes into a white flocculent substance or a resinous mass, called *disacryl* or *disacryl-resin*. When acrolein is heated with alcohol and acetic acid, it is converted into *triethylhydrin* :—



When ammonia is passed into an ethereal solution of acrolein a white amorphous powder called *acrolein-ammonia* $(C_3H_4O)_2NH_3$ is precipitated.

It also combines with hydrochloric acid, forming a crystalline compound $C_3H_4O.HCl$, which on distillation with an alkali is converted into a polymeride of acrolein called *metacrolein*, forming beautiful crystals, which by the action of heat or acids are reconverted into acrolein.

Acrolein hydrochloride yields, by the action of hydrochloric acid, trichlorhydrin and water. When acrolein is treated with phosphorus pentachloride two isomerides are formed, one being *dichloroglycide* and the second has been called *acrol dichloride* $C_3H_4Cl_2$. Nascent hydrogen converts acrolein into allyl alcohol.

Acrylic Acid $C_3H_4O_2$ is produced by adding silver oxide to an aqueous solution of acrolein and allowing the mixture to stand for a few days :—

$$2C_3H_4O + 3Ag_2O = 2C_3H_3AgO_2 + H_2O + 4Ag$$

The acid is not formed by the direct oxidation of the alcohol, the latter being nearly completely destroyed; but it has been produced by combining allyl alcohol with bromine, oxidizing the bibromopropyl alcohol with nitric acid, and heating the bibromopropionic acid with zinc dust and water :—

$$C_3H_4Br_2O_2 + Zn = C_3H_4O_2 + ZnBr_2$$

Acrylic acid is conveniently prepared by heating β iodopropionic acid with sodium ethylate:—

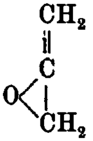
$$C_3H_5IO_2 + 2C_2H_5.ONa = C_3H_3NaO_2 + 2C_2H_5.OH + NaI$$

Or more simply still by distilling β iodopropionic acid with lead oxide:—

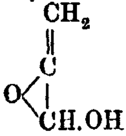
$$2C_3H_5IO_2 + PbO = 2C_3H_4O_2 + PbI_2 + H_2O$$

Acrylic acid is also formed by the dry distillation of hydracrylic acid. These reactions show that acrylic acid as well as its aldehyde must have a constitution analogous to that of hydracrylic acid and β iodopropionic acid:—

Acrolein.



Acrylic Acid.



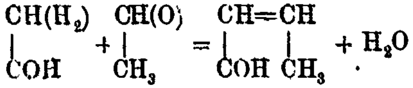
This formula of acrolein appears the more probable as it does not combine with the acid sulphites of the alkali-metals like other aldehydes, from which it also differs by being acted upon by ammonia in quite a different way than the aldehydes of the fatty acids.

Acrylic acid is a limpid liquid, possessing a sour, pungent smell and boiling at 142°. Its most characteristic salt is *lead acrylate* $(C_3H_3O_2)Pb$, crystallizing from hot water in long silky needles.

Ethyl Acrylate $\left.\begin{matrix}C_2H_5\\C_3H_3O\end{matrix}\right\}O$ is produced by the action of zinc, and dilute sulphuric acid on ethyl dibromopropionate. It is a limpid liquid, boiling at 100°, and possessing a very penetrating but not disagreeable odour.

Crotonic Acid $\left.\begin{matrix}C_4H_5O\\H\end{matrix}\right\}O$.—The oil of *Croton Tiglium* consists of glycerides of several solid and liquid fatty acids, and acids of the acrylic series. The crotonic acid contained in it is an oily liquid, which has not been much studied.

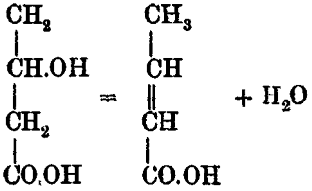
Another solid crotonic acid which has been obtained by synthesis is much better known. Its aldehyde is formed when acetaldehyde is heated with an aqueous solution of zinc chloride:—



$$\begin{matrix}CH(H_2)\\|\\COH\end{matrix} + \begin{matrix}CH(O)\\|\\CH_3\end{matrix} = \begin{matrix}CH{=}CH\\|\quad\quad|\\COH\;CH_3\end{matrix} + H_2O$$

Crotonaldehyde is a limpid liquid having a sharp pungent smell and boiling at 104°. When exposed to the air, it is soon oxidized to crotonic acid.

The same acid is produced by the action of alkalis upon crotonitrile (see Allyl Cyanide), and by the dry distillation of β oxybutyric acid :—



$$\begin{array}{lcll} CH_2 & & CH_3 & \\ | & & | & \\ CH.OH & & CH & \\ | & = & \| & + H_2O \\ CH_2 & & CH & \\ | & & | & \\ CO.OH & & CO.OH & \end{array}$$

Crotonic acid forms large transparent crystals or woolly needles, melting at 72°, and boiling at 182°. When it is fused with caustic potash, it is resolved into two molecules of acetic acid. This decomposition, as well as the synthetical formation of this acid from acetaldehyde, shows that the two middle atoms of the carbon-chain are linked together by two of their combining units, whilst from its formation from allyl-compounds it might have been expected that it had the constitution $CH_2{=}CH{-}CH_2{-}CO.OH$. Such a compound would, however, like the allyl-compounds, yield on oxidation no acetic acid, which is obtained in quantity on oxidizing crotonic acid as well as its nitrile. From this it appears that the latter compound is formed in the following way :—

$$CH_2{=}CH{-}CH_2I + KCN = CH_3{-}CH{=}CH{-}CN + KI$$

This reaction corresponds to the formation of ethyl-vinyl (see page 216).

Crotonic acid combines with nascent hydrogen, forming butyric acid, and it also unites with bromine, yielding an isomeride of the dibromobutyric acid, which is formed by substitution in butyric acid. When the brominated acid is boiled with an alkali, it is converted into monobromocrotonic acid.

Trichlorocrotonaldehyde or Crotonchloral $C_4H_3Cl_3O$.—By acting with chlorine on acetaldehyde, first crotonaldehyde is formed, which by the further action of chlorine is converted into crotonchloral. It is a colourless oily liquid, boiling at 164°, and having a pungent smell. It readily combines with water, forming *crotonchloral hydrate* $C_4H_3Cl_3(OH)_2$, which crystallizes from hot water in silky thin plates melting at 78° ; its vapour is very irritating, and attacks the eyes and mucous membranes.

Trichlorocrotonic Acid $C_4H_3Cl_3O_2$ is obtained by oxidizing crotonchloral with concentrated nitric acid: it crystallizes in needles, melting at 44°, and boiling at 235°. By treating it with zinc and hydrochloric acid it is reduced to *monochlorocrotonic acid* $C_4H_5ClO_2$, crystallizing from hot water in long white needles melting at 100°, boiling at 212°, and possessing an aromatic smell. When sodium amalgam is added to a concentrated solution of its sodium salt, the chlorine is replaced by hydrogen and crotonic acid is formed.

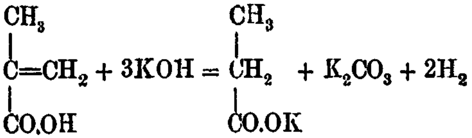
Another monochlorocrotonic acid, melting at 94°, and boiling at about 208°, is formed, together with the isomeric *monochloroquartenic acid*, by acting with phosphorus pentachloride on ethyl acetonecarbonate (so called diethylacetic acid); ethyl chloride and hydrochloric acid are given off, and the residue contains besides phosphorus oxychloride, the chlorides of the two acids. On distilling it with water, monochloroquartenic acid, being the most volatile, distils first; it is an oily liquid, which with sodium amalgam and water yields *quartenic acid* $C_4H_6O_2$, an oily liquid smelling like butyric acid, and boiling at 172°. On fusing it with potash it yields, like crotonic acid, only acetic acid.

Tetrolic Acid $C_4H_4O_2$ is produced by digesting the second monochlorocrotonic acid with potash:—

$$C_4H_5ClO_2 = HCl + C_4H_4O_2$$

It crystallizes in deliquescent, colourless, transparent, rhombic plates, melting at 76°·5, and boiling at 203°. The first modification of monochlorocrotonic acid is not acted upon by potash.

Methacrylic Acid $C_4H_6O_2$.—The ethyl-ether of this third isomeric acid is obtained by treating ethyl oxy-isobutyrate with phosphorus trichloride. The acid is an oily liquid which by fusion with caustic potash is resolved into carbon dioxide and propionic acid:—



$$\begin{array}{l}CH_3\\ |\\ C{=}CH_2\\ |\\ CO.OH\end{array} + 3KOH = \begin{array}{l}CH_3\\ |\\ CH_2\\ |\\ CO.OK\end{array} + K_2CO_3 + 2H_2$$

Angelic Acid $C_5H_8O_2$ is found, together with acetic acid and valerianic acid, in the root of *Angelica Archangelica* and other umbelliferæ. The root is boiled with milk of lime, and the concentrated filtrate distilled with sulphuric acid. The distillate after being neutralized with soda-crystals is evaporated, and the concentrated liquid again distilled with sulphuric acid. On allowing the filtrate to stand for some time, angelic acid separates out in large crystals.

After the acid has been purified by crystallization it melts at 45°, and boils at 191°; it possesses a peculiar, aromatic odour.

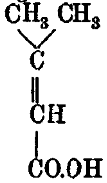
By fusion with caustic potash it is resolved into acetic acid and propionic acid; and by heating with hydriodic acid and phosphorus to 200°, it is converted into valerianic acid.

Angelicaldehyde C_5H_8O is contained, together with a hydrocarbon $C_{10}H_{16}$, in the oil of chamomile (*Anthemis nobilis*). It has not yet been obtained in a pure state, as the hydrocarbon cannot be separated by distillation, and the aldehyde does not form crystalline compounds with the acid sulphites of the alkali-metals. When the oil is heated with caustic potash the hydrocarbon volatilizes, and potassium angelate is formed:—

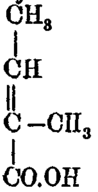
$$C_5H_8O + KOH = C_5H_7KO_2 + H_2$$

Methylcrotonic Acid.—This isomeride of angelic acid is produced by the action of phosphorus trichloride upon ethyl ethomethoxalate; it crystallizes in needles, melting at 62°. When it is fused with caustic potash it yields the same products as angelic acid, the constitution of the two acids being as follows:—

Angelic Acid.



Methylcrotonic Acid.



An acid having the same composition, called *tiglic acid*, has been found in croton-oil; it melts at 64° and boils at 201°. The action of caustic potash on this body has not yet been tried; it is probably identical with methylcrotonic acid, both having the same melting-point, and both their ethyl-ethers boiling at 156°.

Pyroterebic Acid $C_6H_{10}O_2$ has been obtained by the distillation of terebic acid $C_7H_{10}O_4$ (an oxidation-product of oil of turpentine). It is a liquid boiling at 210°, and smelling like butyric acid. It is isomeric with *ethylcrotonic acid*, which has been prepared from ethyl ethoxalate, and crystallizes in quadratic prisms melting at 39°·5. By the action of caustic potash, both acids yield acetic acid and butyric acid.

Cimicic Acid $C_{15}H_{28}O_2$, a crystalline solid melting at 44°, and having a rancid odour, is contained in a kind of tree-bug (*Rhaphigaster punctipennis*).

Hypogœic Acid or Physetoleic Acid $C_{16}H_{30}O_2$ occurs as glyceride, together with palmitic and arachidic acids, in the oil of the earth-nut (*Arachis hypogæa*), and in the oil contained in the cavities of the head of the sperm-whale (*Physeter macrocephalus*). It crystallizes in colourless needles, melting at 34°. In contact with the air it absorbs oxygen, and assumes a yellow colour and a rancid smell. Nitric trioxide converts this acid into an isomeric (or polymeric modification) called *gaïdic acid*, a crystalline colourless mass, which melts at 38°, and remains unaltered in the air.

Both acids combine with one molecule of bromine. By heating these brominated acids with alcoholic potash-solution to 170° they lose hydrobromic acid and are converted into *palmitolic acid* $C_{16}H_{28}O_2$, crystallizing in silky needles melting at 42°. This acid readily combines with one or two molecules of bromine, but apparently not with hydrogen. On oxidizing it with fuming nitric acid a part is converted into *palmitoxylic acid* $C_{16}H_{28}O_4$, a monobasic acid crystallizing in colourless plates melting at 67°. Another portion is further oxidized to *suberic acid* and *suberic aldehyde* $C_8H_{14}O_3$, a yellow oily liquid.

Oleïc Acid or Elaïc Acid $C_{18}H_{34}O_2$ exists as trioleïn, the fluid constituent of many fats and oils, in the fat of the pig and goose, in olive-oil, oil of almonds, &c. To prepare the acid the oils are saponified with lead oxide, and the lead salts exhausted with ether, which dissolves only lead oleate. The ethereal solution is shaken with hydrochloric acid, the upper layer removed, and the ether removed by distillation. The impure oleïc acid left behind is dissolved in ammonia, and barium chloride is added, which precipitates barium oleate. After purifying this salt by crystallization from alcohol, it is decomposed in a closed vessel with tartaric acid, and the pure oleïc acid thus obtained is dried in a current of carbon dioxide, in order to prevent oxidation. Large quantities of impure oleïc acid are now obtained as a by-product in the manufacture of stearin-candles. If this crude acid does not contain a large quantity of oxidation-products, it may be purified by cooling it down to $-7°$, and subjecting the crystals which separate out to strong pressure. The residue is again melted and cooled down, and well pressed, and this operation repeated if necessary. Thus a pure acid is obtained, which may be recrystallized from alcohol.

Pure oleïc acid is a colourless oil solidifying at a low temperature to crystals melting at 14°. From alcohol it crystallizes in brilliant white needles. The perfectly pure acid remains unaltered in the air, but in an impure state it rapidly absorbs oxygen, assuming a yellow colour and rancid smell, and losing the property to crystallize. It volatilizes with overheated steam or *in vacuo*, without decomposition; but under the ordinary atmospheric pressure it is decomposed on heating, yielding fatty acids, such as acetic acid and caprylic acid, and a large quantity of sebacic acid. When it is heated with caustic potash, it is resolved into acetic acid and palmitic acid.

By passing nitric trioxide into cold oleïc acid it is converted into the isomeric *elaïdic acid*, a solid mass, crystallizing from an alcoholic solution in shining scales, melting at 45°. It is stable in the air, and can be volatilized without decomposition. Trioleïn is also converted by nitric trioxide into solid *trielaïdin*. If, therefore, this gas be passed into oil of olives or almonds, they solidify to a crystalline mass. We are not yet able to explain the singular action of nitrous trioxide upon oleïc acid and other acids of this series.

Oleïc and elaïdic acids unite with one molecule of bromine. *Oleïc dibromide* is a heavy, thick yellow oil; by treating it with a cold alcoholic potash solution, *monobromoleïc acid* $C_{18}H_{33}BrO_2$, a crystalline substance, is obtained, which by the action of nascent hydrogen is again converted into oleïc acid.

By the action of a hot alcoholic potash-solution on monobromoleïc acid or on the dibromide all the bromine is taken out, and *stearolic acid* $C_{18}H_{32}O_2$ is formed, which crystallizes in silky needles melting at 48°, and volatilizing on heating without decomposition. It unites with one or two molecules of bromine; fuming nitric acid oxidizes it to *stearoxylic acid*, *azelaïc acid* and *azelaïc aldehyde*.

Stearoxylic Acid $C_{18}H_{32}O_4$ crystallizes in shining plates, melting at 86°; it is a monobasic acid.

Azelaïc Aldehyde $C_9H_{16}O_3$ is a thin, oily liquid possessing an ethereal smell. By the action of bromine and water, or nitric acid, it is oxidized to azelaïc acid.

When stearolic acid is fused with caustic potash, it is first converted into an acid having the composition of *hypogæic acid* $C_{16}H_{30}O_2$, and by the further action of the potash it is converted into *myristic acid* $C_{14}H_{28}O_2$. These reactions prove that stearolic acid contains the group $C{=}C$ twice.

Erucic Acid $C_{22}H_{42}O_2$ occurs in colza-oil and the fatty oil of mustard-seed, and may be obtained from these oils in the same way as oleïc acid is prepared from oil of almonds. It crystallizes in long needles, melting at 34°. With nitric trioxide and bromine it behaves like oleïc acid. By acting with caustic potash on its dibromide, *behenolic acid* $C_{22}H_{40}O_2$ is formed, which is oxidized by fuming nitric acid to *behenoxylic acid* $C_{22}H_{40}O_4$, *brassic acid* $C_{11}H_{20}O_4$, and *brassic aldehyde* $C_{11}H_{20}O_3$.

The following acids are nearly related to those of the oleïc-series:—

Sorbic Acid $C_6H_8O_2$ occurs in the berries of the mountain ash. On distilling their juice, impure sorbic acid passes over as an oily liquid, from which, by treating it with alkalis and decomposing the salt with acids, the pure compound is obtained. It crystallizes in long needles, melting at 134°·5 and distilling at 228°, with partial decomposition. Nascent hydrogen converts it into *hydrosorbic acid* $C_6H_{10}O_2$, a colourless liquid, boiling at 204°·5 and possessing a sweetish smell. It is isomeric with pyroterebic acid and ethylcrotonic acid, and is resolved by fusion with caustic potash into butyric acid and carbon dioxide.

Ricinoleïc Acid $C_{18}H_{34}O_3$ is found as glyceride in castor-oil, and can be obtained from it by the same process by which oleïc acid is prepared from oil of almonds. It is a colourless oil, solidifying at 0° to a crystallized mass. Nitric trioxide converts it into solid *ricinelaïdic acid.*

When this acid or castor-oil soap is fused with caustic soda, hydrogen is evolved, and methyl-hexyl carbinol and sebacic acid are formed:—

$$C_{18}H_{34}O_3 + 2NaOH = C_8H_{18}O + C_{10}H_{16}O_4Na_2 + H_2$$

Ricinoleïc acid has therefore probably the following constitution:—

$$HCO_2.C_8H_{16}.CO.CH\left\{\begin{array}{l}CH_3\\C_6H_{13}\end{array}\right.$$

Linoleïc Acid.—This acid has great resemblance to oleïc acid, and occurs in drying oils, such as linseed-oil, poppy-oil, walnut-oil, &c. It has been very little studied. Its formula appears to be $C_{16}H_{28}O_2$.

TETRAD RADICALS AND THEIR COMPOUNDS.

HYDROCARBONS OF THE ACETYLENE SERIES.

		Boiling-point.			Boiling-point.
Acetylene . .	$C_2 H_2$	—			
Allylene . . .	$C_3 H_4$	—			
Crotonylene .	$C_4 H_6$	18°			
Valerylene . .	$C_5 H_8$	45			
Hexoylene . .	$C_6 H_{10}$	80	Diallyl . . .	$C_6 H_{10}$	59°
Œnanthylidene	$C_7 H_{12}$	107			
Caprylidene .	$C_8 H_{14}$	133			
Decenylene .	$C_{10}H_{18}$	165	Rutylene . .	$C_{10}H_{18}$	150
Benylene . .	$C_{15}H_{28}$	225			
Cetenylene . .	$C_{16}H_{30}$	280			

These hydrocarbons stand in a similar relation to the non-saturated monad radicals of the allyl series as the olefines to the saturated alcohol radicals.

A general method for preparing these compounds consists in heating the dibromides or the di-iodides of the olefines with an alcoholic solution of potash, the reaction taking place in two stages. First a monobrominated olefine is formed—

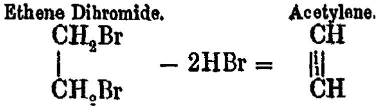
$$C_2H_4Br_2 + KOH = C_2H_3Br + H_2O + KBr$$

which by the further action of caustic potash again loses hydrobromic acid:—

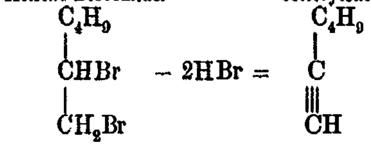
$$C_2H_3Br + KOH = C_2H_2 + H_2O + KBr$$

These hydrocarbons readily combine with one molecule of the elements of the chlorine-group and their hydracids, forming non-saturated compounds, which are capable of combining again with these bodies. The hydrocarbons of this series are therefore tetrad radicals.

Theory points out the existence of a great number of isomerides, but, as the table shows, only very few are known. Those contained in the first column have been prepared by abstracting two molecules of hydrobromic acid from the dibromides of the olefines, and this reaction explains their constitution:—



$$\begin{array}{c} \text{Ethene Dibromide.} \\ CH_2Br \\ | \\ CH_2Br \end{array} - 2HBr = \begin{array}{c} \text{Acetylene.} \\ CH \\ ||| \\ CH \end{array}$$



Hexene Dibromide. Hexoylene.

$$\begin{matrix}C_4H_9\\ | \\ CHBr\\ | \\ CH_2Br\end{matrix} - 2HBr = \begin{matrix}C_4H_9\\ | \\ C\\ ||| \\ CH\end{matrix}$$

Acetylene or Ethine C_2H_2.—This gas is the only hydrocarbon which has been obtained by the direct union of its elements; it is produced when an electric arc from a powerful galvanic battery passes between carbon-poles in an atmosphere of hydrogen. Acetylene is always formed when bodies containing carbon and hydrogen are burnt in a limited supply of air, and also in the decomposition of many hydrocarbons by the electric spark or heat, and it occurs therefore in coal-gas. Acetylene has also been obtained by the electrolysis of the potassium salts of fumaric and maleic acids:—

$$C_2H_2\left\{\begin{matrix}CO_2H\\CO_2H\end{matrix}\right. = CH_2 + 2CO_2 + H_2$$

Pure acetylene is prepared by heating ethene dibromide with alcoholic potash, and passing the vapour through a hot solution of potash in alcohol; it may also be readily obtained by heating chloroform with sodium:—

$$2CHCl_3 + 3Na_2 = C_2H_2 + 6NaCl$$

Impure acetylene is produced in quantity by lighting the gas in a *Bunsen's* burner at the small orifice in the lower end of the tube, an incomplete combustion taking place, and acetylene is formed.

Acetylene is a colourless gas, possessing a strong disagreeable odour; the smell perceived when a *Bunsen's* burner burns down being due to acetylene. It is readily inflammable, burning with a smoky flame, and is tolerably soluble in water.

When it is mixed with chlorine in the diffuse daylight, an explosion generally takes place and carbon separates out, but sometimes the two gases combine quietly, and form the compounds $C_2H_2Cl_2$ and $C_2H_2Cl_4$, which are oily, heavy liquids. It forms also two liquid compounds with bromine, viz. $C_2H_2Br_2$ and $C_2H_2Br_4$, the latter being identical with *bibromethene dibromide.* By heating acetylene with iodine to 100° they combine to *acetylene di-iodide* $C_2H_2I_2$, forming colourless crystals melting at 70°. With hydriodic acid it forms two liquid compounds, C_2H_3I and $C_2H_4I_2$; the latter being isomeric with ethene di-iodide.

Acetylene forms a series of characteristic metallic derivatives. When it is passed over fused potassium, hydrogen is given off, and the bodies C_2HK and C_2K_2 are formed; both are black powders, which are violently decomposed by water, with the re-formation of acetylene. A similar calcium-compound has been obtained by heating an alloy of zinc and calcium with charcoal to whiteness; the resulting black mass yields, with water, quicklime and acetylene:—

$$C_2Ca + 2H_2O = C_2H_2 + Ca(OH)_2$$

The least trace of acetylene can be detected by passing a gas containing it through an ammoniacal solution of cuprous chloride, a blood-red precipitate of *cuproso-ethenyl oxide* $\left.\begin{matrix}C_2HCu_2\\C_2HCu_2\end{matrix}\right\}O$ being formed:—

$$(1)\quad C_2H_2 + Cu_2Cl_2 + NH_3 = C_2HCu_2Cl + NH_4Cl$$

$$(2)\quad 2(C_2HCu_2Cl) + 2NH_3 + H_2O = (C_2HCu_2)_2O + 2NH_4Cl$$

Cuproso-ethenyl Chloride C_2HCu_2Cl is a similar precipitate, which is produced by passing acetylene into a solution of cuprous chloride in potassium chloride.

Argento-ethenyl Chloride C_2HAg_2Cl is formed by the action of acetylene on an ammoniacal solution of silver chloride; it is a white precipitate; the corresponding oxide $(C_2HAg_2)_2O$ is a similar body, which is obtained by passing the gas through a solution of silver nitrate in ammonia.

These copper- and silver-compounds are explosive, decomposing with detonation by percussion; they are decomposed by hydrochloric acid, pure acetylene being evolved, and are therefore used for obtaining this gas in a state of great purity. A very simple method for obtaining pure acetylene consists in placing a gas-burner in which the gas is burning down under a funnel which is connected with an aspirator by which the products of combustion are passed through an ammoniacal silver-solution. The white precipitate is then decomposed by hydrochloric acid, and the resulting silver chloride dissolved in ammonia and used for a new operation:—

$$C_2HAg_2Cl + HCl = C_2H_2 + 2AgCl$$

Nascent hydrogen converts acetylene into ethene; this reduction is effected by acting with zinc and ammonia on the copper-compounds of acetylene:—

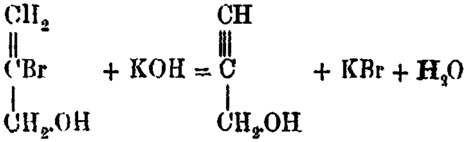
$$C_2HCu_2Cl + NH_3 + 2H_2O + 2Zn = C_2H_4 + NH_4Cl + Cu_2 + 2ZnO$$

When acetylene is shaken with concentrated sulphuric acid, the gas is slowly absorbed, and *ethenylsulphuric acid* $C_2H_3.SO_4H$ is formed. On distilling this acid with water, *ethenyl* or *vinyl alcohol* $C_2H_3.OH$ is obtained; it is a very volatile liquid, which is homologous with allyl alcohol, but has scarcely been examined.

Monobromacetylene C_2HBr.—When a monobromethene dibromide is heated with alcoholic potash, a gas is evolved, taking fire in contact with the air, and consisting of a mixture of acetylene and monobromacetylene.

Allylene or *Propine* C_3H_4 is a gas resembling acetylene; it is prepared by heating monobromopropene or propene dibromide with alcoholic potash. By passing it through an ammoniacal solution of cuprous chloride a greenish-yellow precipitate is formed. *Silver-propinyl* C_3H_3Ag is a white explosive precipitate, which is readily decomposed by hydrochloric acid; it is formed by the action of propine on an ammoniacal silver-solution.

Propinyl Alcohol $C_3H_3.OH$.—This compound, commonly called propargyl alcohol, is produced by acting with caustic potash on monobromallyl alcohol:—



$$\begin{matrix} CH_2 \\ \| \\ CBr \\ | \\ CH_2.OH \end{matrix} + KOH = \begin{matrix} CH \\ ||| \\ C \\ | \\ CH_2.OH \end{matrix} + KBr + H_2O$$

It is a limpid, mobile liquid, boiling at 115°, possessing an agreeable odour, and producing explosive precipitates in an ammoniacal solution of cuprous chloride and an aqueous solution of silver nitrate. The copper compound $Cu_2(C_3H_2.OH)_2$ has a yellow colour, and the silver-compound $AgC_3H_2.OH$ is white.

Propinyl-ethyl ether $\left.\begin{matrix} C_3H_3 \\ C_2H_5 \end{matrix}\right\}O$ has been produced by boiling allylene dibromide or propenyl tribromide with alcoholic potash:—

$$C_3H_4Br_2 + C_2H_5.OH + 2KOH = \left.\begin{matrix} C_3H_3 \\ C_2H_5 \end{matrix}\right\}O + 2KBr + 2H_2O$$

It has also been prepared from monobromallyl-ethyl ether:—

$$\left.\begin{matrix} C_3H_4Br \\ C_2H_5 \end{matrix}\right\}O + KOH = \left.\begin{matrix} C_3H_3 \\ C_2H_5 \end{matrix}\right\}O + KBr + H_2O$$

It is a mobile limpid liquid, boiling at 80°, and precipitating ammoniacal silver- and copper-solutions. The silver-compound $\left.\begin{matrix} C_3H_2Ag \\ C_2H_5 \end{matrix}\right\}O$ is a white crystalline powder, which burns with a flash, like gunpowder.

Crotonylene or *butine*, *valerylene*, and *hexoylene* or *hexine* have been obtained from the dibromides of butene, amylene, and hexene; they are liquids having a strong smell, like acetylene and allylene, but, unlike the latter, they do not form metallic compounds.

Diallyl or *isohexine* C_6H_{10} is prepared by the action of sodium on allyl iodide It is a mobile liquid boiling at 59°, and possessing a pungent odour. It combines with bromine and iodine, forming *isohexine tetrabromide* $C_6H_{10}Br_4$, and *isohexine tetra-iodide* $C_6H_{10}I_4$; both are solid, crystalline bodies. *Isohexine tetranitrite* $C_6H_{10}(NO_2)_4$ is readily formed by the direct union of diallyl and nitrogen tetroxide; it is a white crystalline substance. *Isohexine dichlordihydrate*

$C_6H_{10}\left\{\begin{array}{l}Cl_2\\(OH)_2\end{array}\right.$ is produced by shaking diallyl with an aqueous solution of hypochlorous acid.

When diallyl is heated with concentrated hydriodic acid, the compound $C_6H_{12}I_2$ is obtained as a heavy, oily liquid; on heating this body with silver acetate it is converted into *isohexene diacetate*, which is isomeric with hexene diacetate, and yields with caustic potash *isohexene alcohol* $C_6H_{12}(OH)_2$, a liquid which is soluble in water and boils at about 212°.

Diallyl dissolves in cold concentrated sulphuric acid to a clear liquid; on addition of water, *isohexene oxide* $C_6H_{12}O$ separates out as a light limpid liquid, boiling at 95°, and possessing an ethereal and refreshing smell resembling that of peppermint.

Diallyl or isohexine is isomeric with hexoylene or hexine; the constitution of these two hydrocarbons is represented by the following formulæ:—

$$\begin{array}{cc}
\text{Hexine.} & \text{Isohexine.}\\
CH_3 & CH_2\\
| & \|\\
CH_2 & CH\\
| & |\\
CH_2 & CH_2\\
| & |\\
CH_2 & CH_2\\
| & |\\
C & CH\\
||| & \|\\
CH & CH_2
\end{array}$$

Diallylene or Dipropine $CH{\equiv}C-CH_2-C{\equiv}CH$.—This hydrocarbon has been obtained by heating isohexine tetrabromide with alcoholic potash. It is a limpid and very refractive liquid, boiling at 85°, and combining most energetically with bromine. In an aqueous solution of silver nitrate it produces a white amorphous precipitate, which when heated explodes below 100°.

The other members of the acetylene series have been obtained either from the dibromides of the corresponding olefines or from analogous substitution products. Thus œnanthylidene has been formed by acting with potash on œnanthidene dibromide (see page 234); rutylene was prepared from diamylene, and the isomeric decenylene from the dibromo-substitution product of the hydrocarbon $C_{10}H_{22}$, which exists in petroleum.

ERYTHRITE $C_4H_6(OH)_4$.

This compound is the only known alcohol of a tetrad radical; it exists in a sea-weed, called *Protococcus vulgaris*, and as ether of orsellic acid in different kinds of lichens (*Rocella* species).

Erythrite forms large transparent crystals; it dissolves freely in water, and has a sweet taste. At 120° it melts, and at about 300° it volatilizes with partial decomposition.

Erythryl Nitrate $C_4H_6(NO_3)_4$.—This body, which is commonly called *nitro-erythrite*, is obtained in colourless crystals by dissolving erythrite in concentrated nitric acid and precipitating this solution with sulphuric acid. It is very inflammable, burning with a brilliant flame, and detonates violently when struck with a hammer.

Erythric Acid $C_4H_2O_5$.—This monobasic acid is obtained by heating erythrite with common nitric acid, and forms a crystalline and deliquescent mass.

COMPOUNDS OF HEXAD RADICALS.

MANNITE $C_6H_8(OH)_6$.

Mannite is the alcohol of the hexad radicals *mannyl* C_6H_8; it is found in many plants, as celery, many kinds of fungi and seaweed, and in the young sap of the larch, the lime, and several species of ash. The manna-ash (*Fraxinus ornus*) yields a sweet exudation, called *manna*, from which mannite is easily obtained by exhausting it with boiling alcohol; on cooling, mannite separates out, and is purified by recrystallization.

Mannite crystallizes from alcohol in silky needles, and from water in transparent prisms, melting at 165°. It dissolves in five parts of cold water, and very freely in boiling water, and possesses a pleasant sweet taste.

Mannite has also been found in small quantity among the products of lactic and mucous fermentation, and is produced artificially by the action of sodium amalgam on a solution of grape-sugar $C_6H_{11}O_6$.

When mannite is heated with concentrated hydriodic acid and amorphous phosphorus, it is converted into secondary hexyl iodide (see page 166).

Mannitan $C_6H_8O(OH)_4$.—When mannite is heated to 200°, it loses one molecule of water, and mannitan is formed; it is a syrupy mass, which slowly combines with water, mannite being reproduced.

Mannite and mannitan form a large number of compound ethers.

Mannyl Nitrate or *Nitromannite* $C_6H_8(NO_3)_6$ is obtained by dissolving mannite in fuming nitrite acid, and is precipitated by sulphuric acid as a crystalline powder. It is insoluble in water, and crystallizes from alcohol in silky needles. On heating it first melts, and then burns with a flash like gunpowder, but by percussion it decomposes with a violent detonation. Ammonium sulphide and other reducing agents reconvert it into mannite.

Mannylsulphuric Acid $C_6H_8\begin{cases}SO_4H)_3\\(OH)_3\end{cases}$.—This tribasic acid is obtained by dissolving mannite in concentrated sulphuric acid, diluting with water, and neutralizing the solution barium carbonate. By adding to the filtrate just the required quantity of sulphuric acid, a solution of mannylsulphuric acid is formed, having a very sour taste; on heating, it is resolved into mannite and sulphuric acid.

Mannyl Dichlorhydrate or *Dichloromannite* $C_6H_8(OH)_4Cl_2$ is formed by heating mannite with 15 parts of concentrated hydrochloric acid to 100°; it is soluble in water, and forms colourless crystals, melting at 174°. A mixture of concentrated nitric and sulphuric acids converts it into the *chloronitrate* $C_6H_8(NO_3)_4Cl_2$, crystallizing from alcohol in fine needles. When the dichlorhydrate is acted upon by alkalis, it loses hydrochloric acid and yields the compound $C_6H_8O(OH)_3Cl$, a neutral, bitter substance, which is very soluble in water, and by boiling with it for a long time is converted into mannitan. By the prolonged action of hydrochloric acid on the dichlorhydrate it loses water, yielding the body $C_6H_8O(OH)_2Cl_2$ in colourless crystals.

Mannyl Hexacetate $C_6H_8(C_2H_3O_2)_6$ is formed by heating mannite with acetic anhydride; it forms colourless crystals, which are soluble in water and melt at 100°. At the same time the anhydro-compound $C_6H_8O(OH)_2(C_2H_3O_2)_2$ is produced, which is also obtained by heating mannite with glacial acetic acid; it is a colourless syrup, having a bitter taste.

Similar compounds have been prepared by heating mannite with other fatty acids. Thus on acting on it with stearic acid, it yields $C_6H_8O(C_{18}H_{35}O_2)_4$; this tetrastearate or *tetrastearyl-mannitanide* is a fatty mass, and insoluble in water.

DULCITE OR MELAMPYRIN $C_6H_8(OH)_6$.

This isomeride of mannite has been found in *dulcose*, a crystalline substance from Madagascar, the origin of which is unknown; it also occurs in several plants (*Melampyrum nemorosum*, *Rhinanthus Crista-galli*). It forms monoclinic crystals, melting at 182°, and having a faint, sweet taste, being much less soluble in water than mannite. Dulcite has also been obtained from milk-sugar (see Sugars).

The chemical properties of dulcite are very similar to those of mannite. Hydriodic acid converts it into secondary hexyl iodide, which is identical with that from mannite. When it is heated, amorphous *dulcitan* $C_6H_8O(OH)_4$ is formed, and on heating it with acetic acid it yields a great number of neutral compounds, some of which are ethers of dulcite and other ethers of dulcitan. The hexacetate $C_6H_8(C_2H_3O_2)_6$ forms hard crystalline plates, melting at 171°, and subliming at above 200°.

Isodulcite $C_6H_{12}O_5 + H_2O$ has been obtained by boiling quercitrin (see Glucosides) with dilute acids. It forms large transparent crystals, resembling sugar-candy, and melting with loss of water at 105° to 110°. A mixture of nitric and sulphuric acids converts it into the nitrate $C_6H_7(NO_3)_3(OH)_2$, which is only slightly explosive.

Quercite $C_6H_{12}O_5$ exists in acorns, and forms monoclinic crystals, melting at 235° and possessing a sweet taste. By a mixture of nitric and sulphuric acid it yields a resinous and very explosive nitrate.

Pinite $C_6H_{12}O_5$ has been found in a Californian pine (*Pinus lambertiana*); it forms crystalline nodules, which are soluble in water, possess a very sweet taste, and melt without decomposition above 150°.

MANNITIC ACID $C_5H_6(OH)_5.CO_2H$.

This monobasic acid is produced by exposing a moist mixture of mannite and platinum-black for some time to a temperature of 50° to 60°, a part of the mannite at the same time being oxidized to a peculiar kind of sugar called *mannitose* $C_6H_{12}O_6$. Mannitic acid is a gum-like mass, very soluble in water, and forming uncrystallizable salts.

SACCHARIC ACID $C_4H_4(OH)_4\left\{\begin{matrix}CO.OH\\CO.OH\end{matrix}\right.$

Is a product of oxidation of mannite, cane-sugar and other kinds of sugar. To prepare it, one part of cane-sugar is heated with three parts of nitric acid (specific gravity 1·3), and the liquid kept for some time at 50°. After diluting with half a volume of water, the solution is neutralized with potassium carbonate, and then an excess of acetic acid is added. On standing, acid potassium saccharate crystallizes out, which is converted into the neutral salt, and its solution precipitated with cadmium nitrate. The well-washed cadmium saccharate is decomposed by hydrogen sulphide. On evaporating this solution, the acid is left behind as a white amorphous mass, having a very sour taste.

By boiling it with nitric acid, it is oxidized to tartaric acid:—

$$C_4H_4(OH)_4\left\{\begin{matrix}CO.OH\\CO.OH\end{matrix}\right. + 2O_2 = C_2H_2(OH)_2\left\{\begin{matrix}CO.OH\\CO.OH\end{matrix}\right. + 2CO_2 + 2H_2O$$

MUCIC ACID $C_4H_4(OH)_4\left\{\begin{matrix}CO.OH\\CO.OH.\end{matrix}\right.$

This isomeride of saccharic acid is obtained by oxidizing dulcite, milk-sugar, and several kinds of gum. It is best prepared by heating 2·5 parts of milk-sugar with four parts of water and four parts of nitric acid of specific gravity 1·33, until a reaction commences, and then keeping the liquid for half an hour just at the boiling-point. On cooling, mucic acid separates out in small crystals. From the mother-liquor more may be obtained by boiling it with nitric acid. Mucic acid is but sparingly soluble in cold water, and can therefore easily be separated from saccharic acid, which is often produced together with mucic acid by oxidizing several kinds of sugar and gum. By the prolonged action of nitric acid it is oxidized to racemic acid and oxalic acid; hydriodic acid reduces it to adipic acid $C_4H_8(CO.OH)_2$.

When mucic acid is heated with phosphorus pentachloride, it yields the compound $C_4H_2Cl_2(COCl)_2$:—

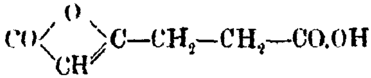
$$C_4H_4(OH)_4\left\{\begin{matrix}CO.OH\\CO.OH\end{matrix}\right. + 6PCl_5 = C_4H_2Cl_2\left\{\begin{matrix}COCl\\COCl\end{matrix}\right. + 6POCl_3 + 8HCl$$

This chloride is decomposed by water, *chloromuconic acid* $C_4H_2Cl_2(CO.OH)_2$ being formed, crystallizing in long white needles. On heating this acid with alcoholic potash to 170°, it is resolved into hydrochloric acid, oxalic acid, and acetic acid.

Hydromuconic acid $C_4H_6(CO.OH)_2$ is obtained by treating chloromuconic acid with water and sodium-amalgam; it crystallizes in white needles, melting at 195°. By the further action of nascent hydrogen it is converted into *adipic acid.* When bromine is added to a solution of hydromuconic acid in glacial acetic acid, it yields *dibromadipic* acid, $C_4H_6Br_2(CO.OH)_2$, crystallizing in small warty needles. On adding silver oxide to its hot aqueous solution, the following reaction takes place:—

$$C_6H_8Br_2O_4 + Ag_2O = C_6H_6O_4 + H_2O + 2AgBr$$

Muconic acid $C_6H_6O_4$ is produced, forming large monoclinic crystals. It is a monobasic acid, which on boiling with baryta water yields carbon dioxide, acetic acid, succinic acid, and other products. The formation as well as the products of decomposition of this acid show that its constitution must be similar to that of aconic acid (page 239), and may be expressed thus:—



PYROMUCIC ACID $C_5H_4O_3$

Is a product of the destructive distillation of mucic acid, but is more conveniently obtained by decomposing its aldehyde with alcoholic potash. Pyromucic acid is a monobasic acid, and crystallizes in flat needles, melting at 134°.

PYROMUCIC ALDEHYDE OR FURFUROL $C_5H_4O_2$

Is a light, oily liquid, boiling at 162°, and possessing a peculiar aromatic odour. It is found amongst the products of destructive distillation of sugar, and is also produced, together with methyl alcohol, when fir-wood is heated with water for a considerable time under a pressure of 100 lb. to the inch. Furfurol is best produced by distilling bran with dilute sulphuric acid; instead of bran, flour, sawdust, or gum may also be used. These bodies contain an insoluble substance, which, when boiled with very dilute sulphuric acid, is converted into a brownish sweet syrup; and this, by distillation with sulphuric acid, yields furfurol. Furfurol combines with the acid sulphites of the alkali-metals, forming crystalline compounds, and reduces an ammoniacal silver-solution.

When furfurol is in contact with aqueous ammonia, it is converted into *furfuramide* $C_{15}H_{12}O_3N_2$, a yellowish-white, crystalline, insoluble substance, which by acids is again resolved into its constituents; whilst, by dilute boiling potash, it is converted into an isomeride, called *furfurine*; it is but sparingly soluble in water, but freely in alcohol; its solution has a strong alkaline reaction. With acids it forms a series of beautifully crystallizable salts, having an intensely bitter taste.

Furfuryl alcohol $C_5H_6O_2$ is produced, together with pyromucic acid, by the action of caustic potash on furfurol:—

$$2C_5H_4O_2 + KOH = C_5H_3KO_3 + C_5H_6O_2$$

It is an oily liquid, which distils at 170°—180° with partial decomposition.

Tetraphenol C_4H_4O is a limpid liquid, boiling at 32°, and having a peculiar smell; it is produced by heating pyromucic acid with alkalies:—

$$2C_4H_3O.COH + KOH = C_4H_3O.CO.OK + C_4H_3O.CH_2.OH$$

Fucusol $C_5H_4O_2$. This isomeride of furfurol has been obtained by boiling seaweeds with dilute sulphuric acid; it is a liquid closely resembling furfurol, both in its physical and chemical properties. It boils at 171°, and yields, with silver oxide and water, *β pyromucic acid* $C_5H_4O_3$, crystallizing in small rhomboidal plates, melting at 130°.

PYRROL C_4H_5N AND CARBOPYRROLAMIDE $C_5H_6ONH_2$.

These two compounds are formed by the destructive distillation of ammonium pyromucate. On evaporation the aqueous portion of the distillate, carbopyrrolamide, is obtained in brilliant plates. By the action of boiling baryta-water it is resolved into ammonia and *carbo-*

pyrrolic acid $C_5H_5NO_2$, which is obtained as a white flocculent precipitate on adding hydrochloric acid to the solution; it crystallizes from alcohol in white prisms, and sublimes at 190° in small feathery crystals. At a high temperature it is resolved into carbon dioxide and pyrrol, which is also readily obtained by heating ammonium pyromucate with glycerin. Pyrrol is a colourless oil, when freshly prepared, but it soon assumes a brown colour; it boils at 133°, and possesses a pleasant smell. Pyrrol has the characteristic property of imparting a fine crimson colour to pine-wood, moistened with hydrochloric acid. This *pyrrol-red* has the empirical formula $C_{12}H_{10}O_2$; it is also obtained as an amorphous precipitate by heating pyrrol with an excess of hydrochloric acid, and by the action of acids on tetraphenol and furfuryl alcohol.

Potassium dissolves in pyrrol with evolution of hydrogen, potassium-pyrrol C_3H_4KN being formed, which, with ethyl iodide, yields *ethyl-pyrrol* $C_3H_4(C_2H_5)N$, a colourless liquid smelling like turpentine; its vapour colours pinewood, moistened with hydrochloric acid like pyrrol.

The constitution of the compounds derived from mucic acid is not exactly known; the relation between them may be expressed by the following formulæ:—

Adipic Acid.	Mucic Acid.	Pyromucic Acid.
$C_4H_8\left\{\begin{matrix}CO.OH\\CO.OH\end{matrix}\right.$	$C_4H_4(OH)_4\left\{\begin{matrix}CO.OH\\CO.OH\end{matrix}\right.$	$C_4H_3O.CO.OH$
Carbopyrrolamide.	Carbopyrrolic Acid.	Pyrrol.
$C_4H_3(NH)CO.NH_2$	$C_4H_3(NH)CO.OH$	$C_4H_4.NH$

CHELIDONIC ACID AND MECONIC ACID.

Chelidonic Acid $C_4H(CO.OH)_3$.—This tribasic acid occurs, together with malic acid, in *Chelidonium majus*, and is obtained by heating the juice of this herb to the boiling-point, filtering and acidifying the liquid with nitric acid. On adding lead-nitrate, a crystalline precipitate of lead, chelidonate, is formed, which is decomposed by hydrogen sulphide. Chelidonic acid is sparingly soluble in cold, but readily in hot water, and crystallizes in colourless needles. By the action of bromine it is decomposed, yielding bromoform and *pentabromacetone* C_3HBr_5O.

Meconic acid $C_4HO(CO.OH)_3$ is found in combination with morphine and other bases in opium; its calcium salt is obtained as a by-product in the manufacture of these alkaloids. On decomposing this salt with hydrochloric acid, impure meconic acid separates out, which is purified by converting it into the ammonium salt, which is crystallized, and then again decomposed with hydrochloric acid.

Meconic acid crystallizes from a hot aqueous solution in scales or prisms containing three molecules of water. The silver salts of this acid are very characteristic. On adding silver nitrate to an aqueous solution of the free acid, the acid salt $C_7Ag_2H_2O_7$ separates out as a white precipitate, which, when boiled for some time with water, is converted into the yellow normal salt $C_7Ag_3HO_7$, which is also produced by precipitating a neutral solution of a meconate with silver-nitrate.

Ferric chloride produces a blood-red colour in a solution of meconic acid, which is not destroyed by the addition of gold chloride, whilst the similar coloration produced by ferric chloride in solutions of sulphocyanates disappears on adding a solution of gold chloride.

Nitric acid oxidizes meconic acid to oxalic acid. By acting with sodium-amalgam on its aqueous solution, it is converted into *hydro-meconic acid* $C_7H_{10}O_7$, an amorphous and deliquescent mass.

Meconic acid is easily resolved into carbon dioxide and *comenic acid* $C_4H_2O(CO_2H)_2$. This decomposition may be effected by heating the acid to 220°, or by boiling it for a long time with water or dilute hydrochloric acid. Comenic acid crystallizes in prisms, which are almost insoluble in cold water, but more freely soluble in boiling water; its aqueous solution gives also a blood-red colour with ferric chloride.

When comenic acid is subjected to destructive distillation, it again loses carbon dioxide, and is converted into *pyrocomenic acid* $C_4H_3O.CO.OH$, forming large transparent plates, which readily sublime, and are freely soluble in water.

CARBO-HYDRATES.

The compounds of this group contain either six atoms of carbon in the molecule, or a multiple of this number, and oxygen or hydrogen always in the same proportion as in water. They are divided into three groups:—

(1) Saccharoses.	(2) Glucoses.	(3) Amyloses.
$C_{12}H_{22}O_{11}$	$C_6H_{12}O_6$	$(C_6H_{10}O_5)_n$
+ Cane Sugar	+ Grape Sugar	+ Starch
+ Milk Sugar	(Dextrose)	+ Glycogen
+ Melitose	− Levulose	+ Dextrin
+ Melizitose	+ Galactose	− Inulin
+ Mycose	− Sorbin	Gums
Synanthrose	− Eucalin	Cellulose
	Inosite	Tunicin

Most of these compounds occur in the vegetable kingdom, forming some of the most important constituents of plants, and a few also occur in the animal organism. The chemical constitution of only a few is known, but that they are nearly related to each other is shown by the fact that most of them can be converted into glucoses by the action of dilute sulphuric acid, The majority of them are optically active, or possess the power of turning the plane of polarization, some to the right hand and some to the left. The right-handed substances are marked in the preceding table with +, and the left-handed with −.

(1) SACCHAROSES.

CANE-SUGAR $C_{12}H_{22}O_{11}$.

Cane-sugar occurs in the juice of many plants, in most sweet fruits, in the nectar of flowers, and in honey. In the greatest abundance it is found in sugar-cane (*Saccharum officinarum*), in *Sorgho saccharatum* (the Asiatic sugar-cane), in beetroot, in sugar-maple, and in several palm-trees.

Sugar is either obtained from sugar-cane or beetroot; smaller quantities are also extracted from sorgho and sugar-maple.

The juice of the sugar-cane is neutralized by a milk of lime and heated to the boiling-point; a coagulum consisting of albuminous matter, phosphates, &c., soon separates out. The clear liquid is quickly evaporated either in open pans, or better *in vacuo*, to the consistency of a thick syrup, and then left to crystallize. The "raw sugar" is drained from the "mother-liquor," which, on further evaporation, yields a second crop of crystals, and a thick brown uncrystallizable syrup called "molasses," or treacle, is left behind.

The raw sugar is sent from the West Indies, &c., to this country, and "refined" by dissolving it in water, adding some lime-water, and filtering the heated liquid through a thick layer of animal charcoal. The colourless filtrate is evaporated in "vacuum-pans" to the crystallizing point, and put into earthen moulds, where it solidifies to a white mass of "loaf-sugar." To obtain "sugar-candy," it is not so far concentrated, and allowed to evaporate quietly and slowly.

Pure cane-sugar crystallizes in large transparent monoclinic prisms, emitting a phosphorescent light when broken in the dark with a hammer. It requires one-third of its weight of cold water, and dissolves in any proportion in boiling water. It is much less easily soluble in dilute alcohol, and almost insoluble in absolute alcohol. It melts at 160° to a clear liquid, which solidifies on cooling to a glassy, amorphous mass of "barley-sugar." When kept for some time this loses its transparency and becomes crystalline. The property of cane-sugar to turn the plane of polarization to the right is made use of for the quantitative determination of sugar in solution, the angle of rotation being exactly proportional to the quantity of sugar contained in layers of equal thickness. The saccharometer of Soleil, an instrument in general use for this purpose, is provided with a graduated circle, divided in such a way that 100 divisions express the rotation caused by a plate of quartz of one millimetre thickness. Now, as exactly the same rotation is produced by a layer of a solution of cane-sugar having a length of 20 centimetres, and containing 164·71 grammes of sugar in one litre, it is only necessary, in order to ascertain the quantity of sugar contained in a substance, to dissolve 164·71 grammes in water, diluting to one litre, and observing the rotation which it produces; the number of divisions being equal to the percentage of sugar.

When sugar is boiled with dilute sulphuric acid, it takes water up, and is resolved into equal parts of dextrose and levulose:—

$$C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6$$

The same decomposition occurs in a solution to which yeast has been added. The solution of these two glucoses turns the polarized light to the left hand, the specific rotatory power of levulose being greater than that of dextrose, and a mixture of these two sugars is therefore called *inverted sugar.*

When sugar is heated above its melting-point, it loses water, and a brown amorphous bitter substance called *caramel* remains behind. At a still higher temperature it blackens; inflammable gases are given off, consisting of marsh-gas, carbon, monoxide, and dioxide; and a distillate is obtained, containing aldehyde, acetic acid, acetone, and furfurol, while porous charcoal is left behind.

Strong sulphuric acid decomposes sugar when heated, and a concentrated sugar solution, even at the common temperature, with copious evolution of sulphur dioxide and formation of a voluminous black carbonaceous mass. The destructive distillation of a mixture of lime and cane-sugar yields marsh-gas, carbon dioxide, acetone, *metacetone* $C_6H_{10}O$, and *isophorone* $C_9H_{14}O$. Metacetone is a colourless liquid, boiling at 84°, and possessing an aromatic smell. On oxidation with chromic acid, it yields carbon dioxide, acetic acid, and propionic acid. Isophorone is an oily liquid, boiling at 210° and having a sweet aromatic odour.

Sugar is an alcohol of an octad radical; by heating it with a large excess of acetic anhydride to 160°, the acetate $C_{12}H_{14}O_3(C_2H_3O_2)_8$ is obtained as a viscid liquid.

Dilute nitric acid oxidizes cane-sugar to saccharic acid, which by further oxidation is converted into tartaric acid and oxalic acid, but by the action of a mixture of strong sulphuric and nitric acid it yields the nitrate $C_{12}H_{18}O_7(NO_3)_4$, which is an amorphous, explosive body.

Cane-sugar forms also metallic compounds; its aqueous solution dissolves caustic lime, baryta, magnesia, and lead oxide: these solutions have a strong alkaline reaction and a bitter taste, and are decomposed by carbon dioxide. Copper oxide and ferric oxide also dissolve in a solution of sugar when an alkali is present; the blue copper solution is slowly decomposed on boiling with the separation of red cuprous oxide. When silver salts or gold salts are heated with a solution of sugar, the metals are reduced to the metallic state.

When an aqueous solution of sugar is saturated with chlorine, and the liquid is then treated with silver oxide, *gluconic acid* $C_6H_{12}O_7$, an isomeride of mannitic acid, is formed. The acid is a sour, syrupy liquid, but the calcium and barium salts crystallize well.

SYNANTHROSE $C_{12}H_{22}O_{11}$

Occurs in the tubers of *Dahlia variabilis*, *Helianthus tuberosum*, and of other Compositæ. It is a light amorphous powder, which is very deliquescent, has no sweet taste, and no action on polarized light. Dilute acids or yeast change it into levulose and dextrose, and on oxidation it yields saccharic acid.

MILK-SUGAR $C_{12}H_{22}O_{11}+H_2O$

Is an important constituent of the milk of mammals, and has also been found together with cane-sugar in the juice of the *Sapodilla* (*Achras sapola*). It is prepared on the large scale, chiefly in Switzerland, by evaporating "whey" to a syrupy state. Milk-sugar forms hard rhombic prisms, losing their water of crystallization at 140°. It dissolves in 6 parts of cold and 2·5 parts of boiling water, and has only a faint sweet taste. When a large quantity of yeast is added to a dilute solution of milk-sugar, fermentation sets in only gradually. By using old cheese as ferment, milk-sugar is converted into lactic acid; at the same time some mannite and alcohol are formed, the latter in larger quantity if the solution be very dilute. When a concentrated solution of milk-sugar is treated with sodium amalgam, a part is reduced to dulcite, and another gives ethyl, isopropyl, and hexyl alcohol.

Nitric acid oxidizes milk-sugar to mucic and saccharic acids, whilst cane-sugar yields only saccharic acid. It also combines with bases like cane-sugar, and reduces an alkaline copper-solution, and solutions of the salts of the noble metals.

When milk-sugar is heated with bromine and water to 100°, it combines with the bromine, forming a compound having probably the formula $C_6H_{12}Br_2O_6$. This body is easily acted upon by silver oxide, and *lactonic acid* $C_6H_{10}O_6$ is formed. This monobasic acid is readily soluble in water, and crystallizes in fine needles; by further oxidation it is converted into mucic acid.

MELITOSE $C_{12}H_{22}O_{11} + 3H_2O$

Is found in a kind of manna which is obtained from various species of Eucalyptus growing in Tasmania. It crystallizes in thin needles, having a faint sweet taste; it is soluble in nine parts of cold and readily in boiling water. When it is heated with dilute sulphuric acid, or in contact with yeast, it is resolved into glucose (probably dextrose), and an isomeric non-fermentable sugar called *eucalin* $C_6H_{12}O_6$.

MELIZITOSE $C_{12}H_{22}O_{11} + H_2O$

Is found in the manna of Briançon, which exudes from the young branches of the larch-tree; it forms small, hard, shining, efflorescent crystals, readily soluble in water, and possessing a sweet taste. By the action of dilute sulphuric acid, it is converted into dextrose.

MYCOSE OR TREHALOSE $C_{12}H_{22}O_{11}$

Forms the chief constituent of *Trehala*, a kind of manna, which is the product of an insect living on an *Echinops* species growing in Syria; and it also occurs in different *fungi*, and the *ergot of rye*. It forms shining, rhombic octahedrons, possessing a very sweet taste, and being freely soluble in water and boiling alcohol. By boiling it with dilute sulphuric acid, it is converted into dextrose.

(2) GLUCOSES $C_6H_{12}O_6$.

DEXTROSE, OR GRAPE-SUGAR.

This sugar is widely diffused through the vegetable kingdom, occurring in most kinds of sweet fruit, as in grapes, in honey, &c. It generally occurs mixed with an equal weight of levulose, or as inverted sugar. It also is found, but in small quantity only, as a normal constituent of blood, yellow of egg, urine, &c. In larger quantity (up to 10 per cent.), it appears in urine in the disease called diabetes.

Pure dextrose may be obtained by exhausting honey with cold alcohol, to dissolve the more soluble levulose, and re-crystallizing the residue from hot alcohol. Dextrose is manufactured on the large scale by boiling starch with very dilute sulphuric acid for several hours, neutralizing the liquid with chalk, and evaporating the solution to crystallization.

Dextrose crystallizes from an aqueous solution with one molecule of water in cauliflower-like masses, and from hot alcohol in warty, anhydrous needles. It is less sweet than cane-sugar, and less soluble in water, requiring about one part of cold water for solution.

Dextrose precipitates from solutions of silver salts the metal, which, if the solution contains free ammonia, separates in form of a brilliant mirror on the sides of the vessel. When it is heated with an alkaline solution of a cupric salt, red cuprous oxide is precipitated. This reaction is made use of for the quantitative determination of grape-sugar. A standard solution (Fehling's solution) is prepared by dissolving 34·64 grammes of crystallized copper sulphate and 200 grammes of Rochelle salt in 600 to 700 cb. cm. of soda-solution (specific gravity 1·2), and diluting with water up to exactly one litre. As one molecule of grape-sugar reduces exactly five molecules of the copper salt, one cb. cm. of the solution corresponds to 0·005 gramme of grape-sugar. The analysis is performed as follows:—10 cb. cm. of the standard solution are placed into a basin, and after being diluted with some water the liquid is heated to the boiling-point, and then the sugar solution added by means of a burette until the blue colour has completely disappeared.

Another simple method is founded on the fact that grape-sugar reduces an alkaline solution of mercuric cyanide to metallic mercury. 10 grammes of pure mercuric cyanide are dissolved in water, 100 cb. cm. of soda-solution (1·145 specific gravity) are added, and the whole diluted with water to one litre. 40 cb. cm. of this solution correspond to 0·1 gramme of sugar. The analysis is performed in the same way as in Fehling's method, and the end of the reaction recognized by bringing a drop of the solution on Swedish filter-paper, and holding it over strong ammonium sulphide, a brown stain being produced as long as any mercuric cyanide remains in solution.

Dextrose melts at 170°, losing water at the same time, and being converted into *glucosan* $C_6H_{10}O_5$, a colourless mass, which is scarcely sweet to the taste, and which by boiling with a dilute mineral acid is reconverted into dextrose. When dextrose is more strongly heated, it yields the same products as cane-sugar.

Concentrated sulphuric acid dissolves dextrose without blackening, *dextrose-sulphuric acid* being formed, the barium salt of which is soluble in water.

Nitric acid oxidizes it to saccharic acid, and by acting on it with chlorine and moist silver oxide *gluconic acid* (page 287) is formed.

By the action of boiling acetic anhydride the diacetate $C_6H_{10}O_6(C_2H_3O)_2$ is obtained as a colourless mass, having a bitter taste; at the same time also the triacetate $C_6H_9O_6(C_2H_3O)_3$ is formed, a similar body which is less soluble in water than the diacetate.

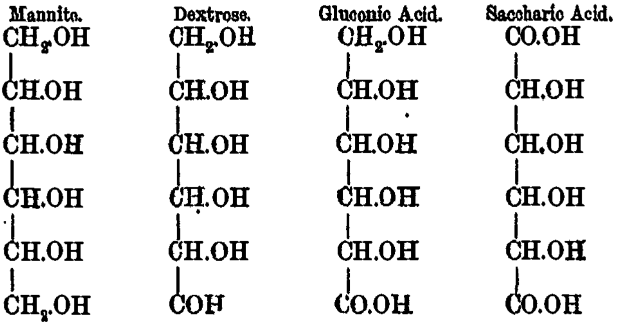
The compounds of dextrose with bases are very unstable bodies. By saturating its solution with lime, a strongly alkaline solution is obtained, which when kept for some time becomes neutral, and contains then the calcium salt of *glucinic acid* $C_{12}H_{18}O_9$: the free acid is a sour, deliquescent, amorphous mass.

Dextrose forms also several compounds with sodium chloride ; of these, that having the composition $C_6H_{12}O_6 + NaCl + H_2O$ is most readily obtained, and forms large crystals.

When yeast is added to a dilute solution of grape-sugar, fermentation soon sets in, the sugar being resolved into carbon dioxide and ethyl alcohol.

By the acting with sodium amalgam on its aqueous solution, it is converted into *mannite;* at the same time some hexyl alcohol is formed together with ethyl alcohol and isopropyl alcohol.

This reaction, together with the fact that dextrose reduces the salts of silver and other metals, shows that this sugar is the first aldehyde of the hexad alcohol mannite. By further oxidation it is converted first into monobasic gluconic acid, and then into bibasic saccharic acid. The connections existing between these bodies appear clearly in the following formulæ :—



$$\begin{array}{cccc} \text{Mannite.} & \text{Dextrose.} & \text{Gluconic Acid.} & \text{Saccharic Acid.} \\ CH_2.OH & CH_2.OH & CH_2.OH & CO.OH \\ | & | & | & | \\ CH.OH & CH.OH & CH.OH & CH.OH \\ | & | & | & | \\ CH.OH & CH.OH & CH.OH & CH.OH \\ | & | & | & | \\ CH.OH & CH.OH & CH.OH & CH.OH \\ | & | & | & | \\ CH.OH & CH.OH & CH.OH & CH.OH \\ | & | & | & | \\ CH_2.OH & COH & CO.OH & CO.OH \end{array}$$

LEVULOSE $C_6H_{12}O_6$

This left-handed sugar is found mixed with dextrose, and often also with cane-sugar in different kinds of fruit, and in honey. As the two glucoses generally occur in equal quantities, they must have been derived from cane-sugar originally contained in the plants, and which by the action of acids or ferments has been transformed into inverted sugar.

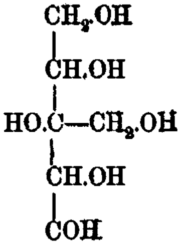
To prepare pure levulose a solution of cane-sugar is heated with dilute sulphuric acid, and the liquid mixed in a mortar with slaked lime, whereby a solid lime-compound of levulose is formed, while that of dextrose remains in solution, and may be removed by strong pressure. The dry residue is decomposed by a solution of oxalic acid, and the filtrate concentrated by evaporation.

Levulose is a colourless uncrystallizable syrup, and is more soluble in water and alcohol than dextrose. It reduces the salts of silver and copper like dextrose, and readily undergoes fermentation in contact with yeast.

On heating, it is converted into *levulosan* $C_6H_{10}O_5$, an amorphous mass, which may be reconverted into levulose by boiling it with a dilute acid.

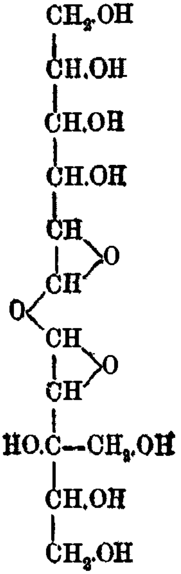
By saturating a dilute solution of levulose with chlorine, and then treating the liquid with silver oxide, no gluconic acid is formed, but *glycollic acid.*

From this it appears that the constitution of levulose is different from that of dextrose; it is also the aldehyde of a hexad alcohol radical, and its constitution may be expressed by the following formula, which at least readily explains why it is easily resolved into glycollic acid:—



$$\begin{array}{c} \mathrm{CH_2.OH} \\ | \\ \mathrm{CH.OH} \\ | \\ \mathrm{HO.C{-}CH_2.OH} \\ | \\ \mathrm{CH.OH} \\ | \\ \mathrm{COH} \end{array}$$

Now, as cane-sugar has to be regarded as an ether, its constitution would be as follows:—



This formula shows that cane-sugar contains the group hydroxyl eight times, a fact which is proved by its forming an acetic ether containing eight acetyls (page 286); and further, it is shown that in cane-sugar the aldehyde-group COH is not present; it acts therefore as reducing agent only after being resolved into dextrose and levulose.

GALACTOSE

Is formed (probably together with dextrose) by boiling milk-sugar with very dilute sulphuric acid. It crystallizes in microscopic prisms, and is readily soluble in water.

It is very easily fermentable, and reduces alkaline copper-solutions like the two other glucoses. From dextrose it differs not only by the greater dextro-rotatory power of its solution, but also by yielding on oxidation only mucic acid (twice as much as the same weight of milk-sugar). When inverted milk-sugar is treated with water and sodium amalgam, it yields *dulcite* and *mannite*.

Besides these three glucoses, we are acquainted with several other varieties, which all possess the property of being readily fermentable. The following bodies, however, differ from the glucoses by not undergoing fermentation in presence of yeast, and by not being converted into a glucose or fermentable sugar by the action of dilute acids.

Sorbin $C_6H_{12}O_6$ occurs in the berries of the mountain-ash, and forms large crystals, having a very sweet taste. When treated with chlorine and silver oxide, it is oxidized to glycollic acid.

Inosite $C_6H_{12}O_6 + 2H_2O$ has been found in the muscular substance of the heart, lungs, liver, kidneys, &c., in green kidney-beans and the unripe fruits of other Papilionaceæ, and also in other plants. It forms large transparent rhombic crystals, which lose their water of crystallization when exposed to the air. It is soluble in water, and has a sweet taste. By the action of dilute nitric acid it is oxidized to oxalic acid, but the concentrated acid converts it into an explosive nitric ether, called *nitro-inosite*. $C_6H_6(NO_3)_6$.

Eucalyn $C_6H_{12}O_6$ is obtained together with ethyl alcohol by the fermentation of melitose, and forms an uncrystallizable syrup:—

$$C_{12}H_{22}O_{11} + H_2O = 2CO_2 + 2C_2H_6O + C_6H_{12}O_6$$

(3) AMYLOSES $(C_6O_{10}H_5)_n$.

STARCH, OR AMYLUM.

This important and widely-diffused body is found to a greater or less extent in nearly every plant. It is most abundant in grain, in rice, and a great many other seeds, and in certain roots and tubes, as in potatoes, and in the stem of several palm-trees.

Starch is a soft, white powder, which under the microscope is seen to be destitute of crystalline structure, being made up of transparent rounded granules, possessing an organized structure. The starch-granules of different plants vary much both in form and magnitude (see Figs. 12 and 13), the average diameter being of—

Potato-starch	0·185 mm.
Sago-starch	0·070 „
Wheat-starch	0·050 „
Starch from *Chenopodium Quinoa*	0·002 „

Starch is insoluble in cold water, and in alcohol and ether. When it is heated with water above 60°, the granules burst, and form a thick mucilaginous mass, called "starch-paste." On boiling starch with a large quantity of water for a long time, the particles become so finely divided, that they pass through filter-paper, and on continuing the boiling a complete solution of starch is effected. When alcohol is added to the clear liquid thus obtained, *soluble starch* is precipitated, a white amorphous powder, which is soluble in cold water.

Both insoluble and soluble starch combine with iodine, forming a deep-blue compound, which, when heated with water, becomes colourless; but on cooling the blue colour appears again. Bromine imparts to starch an orange colour.

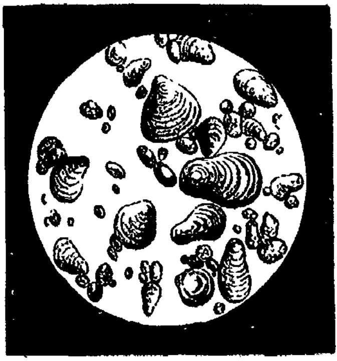


Fig. 12.—Potato-starch.

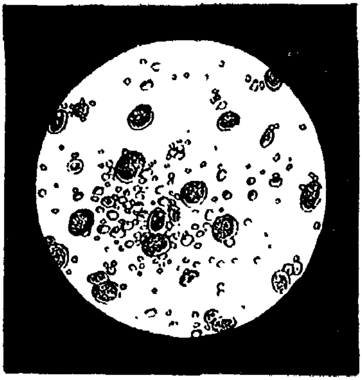


Fig. 13.—Wheat-starch.

A hot solution of starch is precipitated by lime-water, baryta-water, and basic lead acetate, insoluble compounds of starch with the oxides being formed.

Cold concentrated sulphuric acid dissolves starch with the formation of amylum-sulphuric acid. The concentrated nitric acid converts it without the evolution of gases into the nitrate $C_{12}H_{18}O_9.NO_3$ called *xyloïdin*, which on addition of water is precipitated as a white powder. The dry substance burns like gunpowder, and detonates by percussion.

When starch is heated with an excess of acetic anhydride in 140°, it is converted into *hexacetyl-amylum* $C_{12}H_{14}(C_2H_3O)_6O_{10}$, a white amorphous body; which is not coloured blue by iodine, and when treated with alkalis is resolved into starch and acetic acid.

DEXTRIN.

This body, which is also called *British Gum*, is an amorphous white powder or gum-like mass, which is readily soluble in water, and occurs in small quantity in plants and in the flesh. It is obtained by heating starch above 150°, or by exposing starch moistened with dilute hydrochloric or nitric acid to a temperature of 110°. Dextrin is also formed by heating starch-paste to 70°, and adding to it an infusion of malt, or boiling it for a short time with dilute sulphuric acid. The active principle of malt is a ferment called "Diastase," of which a very small quantity is sufficient to convert a very large quantity of starch into dextrin. By the further action of diastase or sulphuric acid upon dextrin, it assimilates water, and is converted into dextrose.

Hexacetyl-dextrin $C_{12}H_{14}(C_2H_3O)_6O_5$ is obtained by heating dextrin or starch with acetyl anhydride to 160°; it is a white amorphous body, insoluble in water, but soluble in glacial acetic acid, and yielding again dextrin by the action of alkalies.

GUMS.

The name gum is used to designate a number of bodies occurring in many plants; they are all amorphous, more or less soluble in water, and insoluble in alcohol; on boiling them with dilute sulphuric acid, they are converted into a glucose.

Gum-arabic and *gum-senegal* are the produce of different kinds of acacia. They form colourless or yellow rounded irregular masses, which are more or less transparent, and dissolve in water to a thick viscid solution. These gums consist of the potash and lime compounds of *Arabin*. To prepare this compound, a little hydrochloric acid is added to a solution of gum-arabic, and the arabin precipitated by alcohol. It is a white, amorphous, tasteless mass, which when dried at 100° has the composition $C_{12}H_{20}O_{10} + H_2O$; at 150° it becomes anhydrous. Nitric acid oxidizes it to mucic and saccharic acids. When arabin is heated with dilute sulphuric acid, it is converted into *arabinose* $C_6H_{12}O_6$, a non-fermentable sugar, crystallizing in rhombic needles, and turning the plane of polarization strongly to the right.

Cerasin is the insoluble part of the gum of the cherry-tree and plum-tree, and is also found together with arabin in beet-root; it forms with cold water a thick, mucilaginous liquid. A similar substance is *gum-tragacanth*.

Mucilage occurs in many plants, as in the kernels of the quince, in linseed, in salep (the roots of orchis species), in the root of the marsh-mallow, &c.; it is soluble in cold water, forming a thick, more or less opaque liquid.

INULIN

Occurs, together with synanthrose (page 287), in the roots of *Inula Helenium*, *Helianthus tuberosus*, &c. It is a light, white powder, which is sparingly soluble in cold water. In hot water it dissolves to a mucilaginous liquid, from which, on cooling, the greater part of inulin is again deposited as powder. Iodine imparts a brown colour to it. By boiling with dilute acids it is converted into levulose.

GLYCOGEN

Is a white, amorphous powder, resembling starch, and occurring in the liver of several animals, and in the tissues of the embryo, in the yolk of egg, and some mollusca. It dissolves in cold water to an opalescent liquid, and gives a brown colour with iodine. By the action of ferments or dilute acids it is readily converted into dextrose.

CELLULOSE, OR LIGNIN,

Forms a large proportion of the solid parts of all plants. The pure substance is readily prepared by treating fine linen or cotton with dilute potash-solution, dilute acids, ether, &c., to remove all adhering impurities. In the pure state it is perfectly white, exhibiting the structure of that part of the plant from which it has been obtained. It is insoluble in water, alcohol, and ether, but readily soluble in a solution of cupric hydroxide in ammonia. On adding an acid to this solution, it is precipitated as an amorphous mass.

Concentrated sulphuric acid dissolves it in the cold; on adding water to this solution, white amorphous flakes separate out, which are coloured blue by iodine, like starch. By the continued action of sulphuric acid, it is converted into dextrin and dextrose.

If unsized paper be dipped for a few seconds in a cold mixture of two volumes of concentrated sulphuric acid and one volume of water, and then washed with water and ammonia, the so-called *parchment paper* is obtained.

By the action of concentrated nitric acid on cellulose, it is without change of form converted into a nitric ether, the composition and properties of which vary according to the mode of preparation.

Gun-cotton $C_{12}H_{14}O_4(NO_3)_6$.—To prepare this body, cotton-wool is first immersed in a boiling dilute solution of potassium carbonate, then washed with water and well dried. It is now steeped for a few minutes in a cold mixture of one part of concentrated nitric acid and three parts of oil of vitriol, then squeezed, and again placed in a fresh acid mixture, and left there for forty-eight hours. It is then again well squeezed, and washed for a long time with running water, and lastly steeped again in a solution of potassium carbonate.

Gun-cotton thus manufactured will keep without change for almost any length of time, and may be kept under water for safety's sake; possessing, after drying, all its original properties.

It is insoluble in water, alcohol, and ether. It takes fire at 150°, burning away rapidly, but without explosion; but when ignited in a confined space, or by percussion, it decomposes with a violent detonation, the action of which equals that of five times its weight of gunpowder. The products of its decomposition consist principally of nitrogen, carbon monoxide, carbon dioxide, and water.

A different product is obtained by steeping cotton-wool in a warm mixture of two parts of dry saltpetre and three parts of concentrated sulphuric acid, for twenty-four hours: the substance thus formed is called soluble gun-cotton, or *collodion-wool*; it is less explosive, and readily soluble in a mixture of ether with a little absolute alcohol, forming a clear solution called *collodion*, which, when left to evaporate, dries up quickly to a thin, transparent, adhesive, waterproof membrane, which is used in surgery as a covering for wounds and burns. Collodion is also largely used in photography to cover glass-plates with a transparent membrane containing silver-salts.

Collodion wool contains less NO_3 than gun-cotton, but its composition is not exactly known; both compounds are reconverted into cotton-wool by acting on them with a solution of a ferrous salt or other reducing agents; hydroxyl replaces the group NO_3, and the latter oxidizes the ferrous salt, and nitric oxide is given off.

By the action of strong nitric acid upon paper, sawdust, flax, &c., explosive bodies resembling gun-cotton are obtained.

Woody fibre does not contain free cellulose but in combination with other bodies. Thus finely-divided pinewood (*Pinus abies*), after being purified by exhausting it with very weak acetic acid, hot water, alcohol, and ether (in order to remove colouring matter, resin, &c.), yields to an ammoniacal solution of cupric oxide only a trace of cellulose. Its composition was found to be $C_{30}H_{46}O_{21}$; on boiling it with hydrochloric acid, dextrose goes in solution, and an insoluble residue of *Lignose* $C_{18}H_{26}O_{11}$ is left behind:—

$$C_3H_{46}O_{21} + 2H_2O = 2C_6H_{12}O_6 + C_{18}H_{20}O_{11}$$

Lignose is also insoluble in an ammoniacal solution of cupric oxide, but is converted into cellulose on boiling it with weak nitric acid; besides cellulose, other products are formed, probably belonging to the aromatic group, as by fusing lignose with caustic potash, *pyrocatechin* $C_6H_6O_2$, a body belonging to this group, is formed.

Pine-wood may therefore be regarded as a kind of ether, containing the radicals of grape-sugar, cellulose and pyrocatechin:—

$$C_{30}H_{46}O_{21} + 2H_2O + O = 2C_6H_{12}O_6 + C_{12}H_{20}O_{10} + C_6H_6O_2$$

The stony concretions of pears principally consist of *glucodrupose* $C_{24}H_{36}O_{16}$, which by boiling with hydrochloric acid yields dextrose and *drupose* $C_{12}H_{20}O_8$; and the latter, when boiled with weak nitric acid, yields cellulose, whilst on fusing it with caustic potash pyrocatechin is formed.

TUNICIN.

This name has been given to a substance which has the greatest resemblance to cellulose, and appears to be identical with it. It occurs in the mantle of Ascidia (spec. of Cynthia, Phallusia, &c.), from which it is obtained by boiling the mantles first with hydrochloric acid, and then with caustic potash. In concentrated sulphuric acid it deliquesces to a colourless liquid, which on boiling with water yields a glucose.

FERMENTATION.

Several kinds of sugar and other bodies undergo, under certain conditions, a peculiar chemical change called *fermentation*. Fermentation is always caused by the presence of a *ferment* or a substance in a peculiar state of decomposition. Although to start fermentation the presence of a ferment is necessary, it does not take part in the decomposition of the fermenting substance. The products of fermentation vary according to the nature of the fermenting body, as well as according to the nature of the ferment. Each peculiar kind of fermentation requires a certain temperature, and it is nearly always accompanied by the development of certain living bodies (infusoria or fungi); but whether the growth of these is a cause or a consequence of the chemical change has not yet been decided.

In many cases fermentation sets in without bringing a ferment in the liquid; thus grape-juice, when exposed to the air, soon begins to ferment, because it contains albuminous substances which, in contact with the air, readily undergo decomposition or putrefaction, and are thus converted into a ferment.

Vinous Fermentation.—When yeast is added to a dilute solution of dextrose or another glucose, vinous fermentation speedily sets in; whilst a solution of cane-sugar undergoes fermentation only slowly, the cause being that this sugar must first be converted into inverted sugar before fermentation can commence. Vinous fermentation does not take place at a temperature below 0° or above 35°, and proceeds most rapidly at 25° to 30°. The presence of a large quantity of acids or alkalis prevents fermentation; while if the liquid has a faint acid reaction, fermentation proceeds best. The chief products of vinous fermentation are ethyl alcohol and carbon dioxide:—

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

A small quantity of sugar is at the same time converted into other products; about 2·5 per cent. being transformed into glycerin and 0·6 to 0·7 into succinic acid.

The yeast which is formed in the fermentation of the juice of grape and other kinds of fruit, and of malt-wort, is produced from soluble albuminous bodies contained in fruit and corn. It consists of one of the lowest members of the vegetable kingdom (*Torula cerevisiæ*), and under the microscope is seen to be made up of little oval, transparent globules, having a diameter of not more than 0·1 mm., and often cohering in clusters and strings. They are propagated by budding, and quickly die as soon as they have reached their highest state of development. In contact with air and water, yeast soon undergoes putrefaction.

Lactic Fermentation.—This kind of fermentation takes place by adding putrefying cheese to a dilute solution of glucoses, cane-sugar, milk-sugar, or gum, and exposing it to a temperature of 25° to 35°.

$$C_6H_{12}O_6 = 2C_3H_6O_3$$

Acids prevent lactic fermentation, and therefore chalk or zinc oxide is added to keep the solution neutral. Together with lactic acid, a certain quantity of mannite is always produced, and also a peculiar microscopic fungus consisting of small globules.

Butyric Fermentation.—When the semi-solid mass of calcium lactate formed in lactic fermentation is exposed to a temperature above 36°, it redissolves, being converted into soluble calcium butyrate. At the same time hydrogen is evolved, and a living microscopic organism having a cylindrical shape and a length of about making its 0·02 mm. appears in the liquid.

Mucic Fermentation.—Under certain conditions which are not quite understood, dextrose undergoes mucic fermentation, the products of which consist of lactic acid, mannite and a kind of gum; a microscopic fungus in the shape of small globules, adhering in rings, making its appearance at the same time.

Other kinds of fermentation will be found under the head of Glucosides.

TERPENES AND CAMPHORS.

This group consists of a number of compounds, containing ten atoms of carbons in the molecule. The *terpenes* are hydrocarbons, having the common formula $C_{10}H_{16}$, and possessing very similar chemical properties, whilst their physical properties vary; the different compounds having different boiling-points, specific gravities, &c. Their odour also varies much, and most of them are optically active; some turning the place of polarization to the right, others to the left. The cause of this *physical* isomerism is not yet known.

The camphors contain oxygen, and most of them exhibit the character of alcohols.

Most of the terpenes, as well as camphors, exist in plants as *essential* or *volatile oils*.

OIL OF TURPENTINE $C_{10}H_{16}$.

All the trees belonging to the order Coniferæ contain resins and liquid hydrocarbons; a mixture of both exudes as an oleo-resinous juice from the barks of these trees, and is called *turpentine*. When turpentine is distilled; either alone or with water, the hydrocarbons volatilize, and resin is left behind.

Oil of turpentine is obtained from different species of *Pinus* and *Abies*; it is a limpid, mobile liquid, with the specific gravity 0.89, and boiling at 160°. It is almost insoluble in water, but readily dissolves in strong alcohol and glacial acetic acid; with ether and absolute alcohol it mixes in any proportion. Oil of turpentine dissolves sulphur, phosphorus, resins, and many other bodies which are insoluble in water. It readily absorbs oxygen, converting it into ozone, which gradually oxidizes the oil, forming resinous products.

The oils of turpentine of different origin exhibit considerable diversities in their optical properties. The French oil (from *Pinus maritima*), as well as the oils from *Pinus Larix* and *Abies pectinata*, turn the plane of polarization to the left, whilst English turpentine-oil (from *Pinus australis*) turns it to the right.

These different varieties are converted into new optical modifications, by repeated distillation or by the action of acids. It also appears that the oil contained in the plants is different from that which is obtained by distillation. Thus, on distilling the young branches of the pine with water, an oil is obtained possessing an agreeable odour, which is changed into that of the common oil by distilling it over potash.

When oil of turpentine is boiled with dilute nitric acid, it is oxidized to acetic acid, propionic acid, butyric acid, oxalic acid, terebic acid, and other compounds. *Terebic acid* $C_7H_{10}O_4$ crystallizes in colourless prisms, and is resolved by heat into carbon dioxide and *pyroterebic acid* $C_6H_{10}O_2$ (see page 270).

Terpin or Hydrate of Turpentine-oil $C_{10}H_{20}O_2 + H_2O$.—Oil of turpentine slowly combines with water, forming terpin; this combination takes place more quickly if an acid be present. To prepare this compound, eight volumes of the oil are mixed with two volumes of weak nitric acid and one volume of alcohol; the mixture is exposed to the sunlight, and frequently shaken. Terpin crystallizes in large rhombic prisms, melting at 100° with loss of one molecule of water; the anhydrous compound sublimes at 150° in needles. It is sparingly soluble in cold water, but dissolves freely in alcohol and in boiling water.

Terpinol $C_{20}H_{34}O$ is obtained by boiling terpin with dilute hydrochloric or sulphuric acids. It is a colourless and very refractive oil, smelling like hyacinths, and boiling with partial decomposition at 168°.

When terpin is heated with alkalis to 400°, it is converted into *terebentic acid* $C_8H_{20}O_2$, crystallizing in small needles, melting at 90°, and boiling at 250°.

Terpene Monohydrochloride $C_{10}H_{17}Cl$.—When hydrochloric acid gas is passed into oil of turpentine, two isomeric hydrochlorides are produced. One, being a solid, crystallizes from hot alcohol in brilliant prisms, melting at 115°, and boiling at a higher temperature with partial decomposition. This body has a strong odour resembling that of camphor; by passing its vapour over quicklime at 200°, it is resolved into hydrochloric acid, and *camphilene* $C_{10}H_{16}$, a liquid which is optically inactive.

The second hydrochloride is a liquid, which by distillation over quicklime yields optically inactive *camphilene* $C_{10}H_{16}$. The liquid compound is easily oxidized by nitric acid, which does not act on the solid modification.

Terpene Dihydrochloride $C_{10}H_{18}Cl_2$ is formed when oil of turpentine is left for several weeks in contact with fuming hydrochloric acid, or when the gaseous acid is passed into terpin or terpinol. It forms colourless crystals, and yields by distillation over quicklime a terpene, smelling like rosemary.

All these different terpenes may again be combined with hydrochloric acid, and the hydrochlorides thus formed are converted into new modifications of turpentine oil by distilling them with quicklime, but all yield at the end one and the same product, called *terebene* $C_{10}H_{16}$. The same body is produced together with *dieterebene* $C_{20}H_{32}$, when oil of turpentine is treated with boron fluoride or strong sulphuric acid. Terebene has also been obtained synthetically from *amylene* C_5H_{10}, which by the action of sulphuric acid is converted into *diamylene* $C_{10}H_{20}$ (page 234). By heating diamylene dibromide with alcoholic potash, it yields *rutylene* $C_{10}H_{18}$, and the dibromide of this hydrocarbon again loses hydrobromic acid by the action of potash, and is converted into terebene.

Terebene is a mobile liquid, boiling at 156°, and smelling like thyme; it is optically inactive, and forms with hydrochloric acid a *semi-hydrochloride* $(C_{10}H_{16})_2ClH$.

By the action of chlorine on oil of turpentine, substitution-products are formed, which are but little known. When chlorine is passed over the solid monohydrochloride, a yellow liquid, $C_{10}H_{12}Cl_4.HCl$, is formed, which easily splits up into hydrochloric acid, and *tetrachloroterpene* $C_{10}H_{12}Cl_4$, colourless crystals melting at 110°.

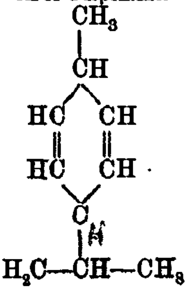
When bromine is added to well-cooled oil of turpentine or terpine, *terpene dibromide* $C_{10}H_{16}Br_2$ is formed; it is a heavy oily liquid, and a very unstable compound, which by heating it with aniline to 180°

loses hydrobromic acid, and is converted into *cymene* $C_{10}H_{14}$, an aromatic hydrocarbon occurring in several volatile oils.

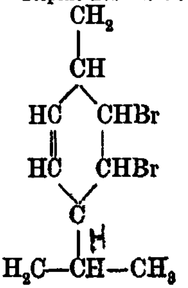
Iodine acts violently on oil of turpentine; when a large quantity is added at once, an explosive reaction takes place, and the liquid frequently takes fire; but by adding the iodine only gradually, and then heating the solution for some time, cymene and hydriodic acid are formed.

This transformation of oil of turpentine into cymene explains its constitution; cymene is *methyl-isopropyl-benzene* (see Aromatic Compounds), and is produced by abstracting two molecules of hydrobromic acid from terpene dibromide: this reaction is explained by the following formulæ:—

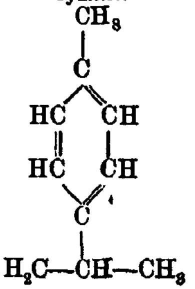
Oil of Turpentine.



Terpene Dibromide.

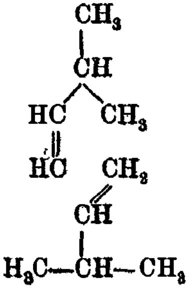


Cymene.

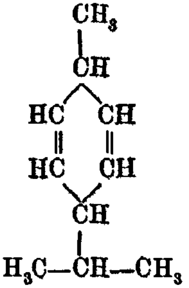


Whether terebene has the same constitution as oil of turpentine is not known; but supposing it was so, the synthesis of this hydrocarbon from amylene may also easily be explained:—

Two molecules of Amylene.



Terebene.



TERPENES FROM CITRUS SPECIES.

These hydrocarbons occur chiefly in the peels of the fruit of these trees, and are distinguished by their fragrant odour.

Lemon-oil from the fruit of *Citrus Limonum* consists principally of *citrene* $C_{10}H_{16}$, boiling at 170°, and turning the plane of polarization to the right. Its chemical properties are very similar to those of turpentine oil; it yields a solid hydrate, and crystalline hydrochlorides. With bromine and aniline it forms cymene. Similar terpenes exist in the *oils of orange-peel, bergamot*, &c.

TERPENES FROM OTHER SOURCES.

These hydrocarbons are found in a great number of volatile oils, some of them consisting only of terpens, such as oils of lavender, juniper, copaiba, cubebs, pepper, elemi, and the camphor-trees. Others are mixtures of terpenes with acids, as oil of valerian; or with aldehydes, as oil of chamomile, which contains angelicaldehyde. A great number of essential oils also contain, besides, terpenes, camphors, cymene, or other aromatic compounds.

CAOUTCHOUC AND GUTTA-PERCHA.

Caoutchouc or *India-rubber* is the dried milky juice of several tropical trees (*Ficus elastica, Jatropha elastica, Siphonia Cahuchu*, &c.). The fresh juice has an acid reaction; on mixing it with water, caoutchouc separates gradually out as a white curdy precipitate, which dries up to a gum-like mass. The black colour of the commercial article is due to the effect of smoke; it may be purified by dissolving it in chloroform, and precipitating the clear solution with spirits of wine. It consists chiefly of a mixture of hydrocarbons, polymeric with the terpenes. It is insoluble in water and alcohol; with ether or petroleum it forms a gelatinous mass, and partially dissolves. It is completely soluble in oil of turpentine, benzene, chloroform, and carbon disulphide. When cold it is hard and tough; on heating it becomes soft and elastic; and at a temperature above the boiling-point of water it melts, but on cooling does not return to the original state, but remains soft and viscid.

It is much used for the manufacture of waterproof and elastic fabrics, for elastic tubing, &c., and is a most valuable substance for the chemists, as it is only affected by a very few chemical agents.

Caoutchouc combines in different proportions with sulphur. The so-called *vulcanized* India-rubber, which is much more elastic than common caoutchouc, is obtained by mixing the latter intimately with sulphur by means of carbon disulphide; it contains about 2 to 3 per cent. of sulphur. By mixing it with about half its weight of sulphur, it is converted into a hard, horny mass, called "Ebonite" or "Vulcanite," which is much used for making combs, disks for electric machines, &c.

By destructive distillation, caoutchouc yields an oily liquid, containing *Isopropene* C_5H_8, boiling at 37°, and *caoutchene* $C_{10}H_{16}$, boiling at 171°.

Gutta-percha is the hardened milky juice of *Isonandra Gutta*, a tree growing in different parts of India. It is harder and less elastic than caoutchouc, but in warm water it becomes quite soft, and can then be formed into any shape. It has the same composition as caoutchouc, and dissolves in the same solvents as the latter. By destructive distillation, it yields isopropene, caoutchene, and a heavy oil called *heveene*, which appears to be polymeric with these other hydrocarbons.

CAMPHORS.

Common Camphor, or *Japan Camphor* $C_{10}H_{16}O$, is obtained in China, and Japan by distilling the branches and leaves of *Laurus Camphora* with water. It is a colourless, crystalline, translucent mass, having a powerful, peculiar odour and taste. By sublimation it may be obtained in brilliant crystals. It melts at 175°, and boils at 204°. Camphor is only sparingly soluble in water, but freely soluble in alcohol and acetic acid. Small pieces thrown on water move about with a revolving motion.

When camphor is heated with concentrated hydriodic acid, several hydrocarbons are formed, as *campholene* C_9H_{18}, a liquid boiling at 135°, and the compounds $C_{16}H_{18}$, boiling at 155°, and $C_{10}H_{20}$. By the action of phosphorus pentasulphide on camphor, *cymene* $C_{10}H_{14}$ (page 300) is formed:—

$$5C_{10}H_{16}O + P_2S_5 = 5C_{10}H_{14} + P_2O_5 + 5SH_2$$

On heating a solution of camphor in toluene with sodium, two compounds, called *sodium-camphor* $C_{10}H_{15}NaO$ and *sodium camphylate* $C_{10}H_{17}NaO$, are produced:—

$$2C_{10}H_{16}O + Na_2 = C_{16}H_{15}NaO + C_{10}H_{17}NaO$$

By the action of methyl iodide on this mixture, the sodium is replaced by methyl, and *methyl-camphor* $\left.\begin{matrix}CH_3\\C_{16}H_{13}\end{matrix}\right\}O$, and *camphyl-methyl ether* $\left.\begin{matrix}CH_3\\C_{10}H_{17}\end{matrix}\right\}O$ are produced. Ethyl iodide acts in an analogous way; *ethyl-camphor* is a liquid boiling at 230°.

When the mixture of the two sodium-compounds is heated in a current of dry carbon dioxide to 100°, the sodium salts of *campho-carbonic acid* $C_{10}H_{15}O.CO_2H$ and of *borneol-carbonic acid* $C_{10}H_{37}O.CO_2$ are formed. On dissolving these salts in water, lactic acid is decomposed, and *borneol* or *camphyl alcohol* $C_{10}H_{18}O$ separates out:—

$$\left.\begin{matrix}C_{10}H_{17}\\Na\end{matrix}\right\}CO_3 + H_2O = C_{10}H_{18}O + \left.\begin{matrix}H\\Na\end{matrix}\right\}CO_3$$

Hydrochloric acid precipitates from the filtrate camphocarbonic acid, which separates from hot alcohol in colourless crystals, melting at 119°, and splitting up at a higher temperature into carbon dioxide and camphor.

Monochlorocamphor $C_{10}H_{15}ClO$ is a colourless, crystalline mass, which has been obtained by the action of hypochlorous acid upon camphor.

Monobromocamphor $C_{10}H_{15}BrO$.—By adding bromine to a solution of camphor in chloroform, *camphor dibromide* $C_{10}H_{16}OBr_2$ is obtained in colourless crystals; it is a very unstable compound, and readily resolves into hydrobromic acid and monobromocamphor, which crystallizes in colourless prisms.

Camphor Nitrate $(C_{10}H_{16}O)_3N_2O_5$.—This remarkable compound is produced together with camphoric acid, when camphor is boiled for some time with nitric acid. It is a thick oily liquid, having a camphor-like and sour smell; water decomposes it into nitric acid and camphor.

Common camphor turns the plane of polarization to the right; a compound having the greatest resemblance to it, but exerting a left-handed rotatory action, is contained in the volatile oil of *Pyrethrum Parthenium*, from which it is deposited at a low temperature as a crystalline mass.

Other isomerides of camphor occur in the volatile oils of artemisia, absinthium, mentha, pulegium, and other labiate plants, and also in the blue oils of chamomile and galbanum.

Borneol, Borneo Camphor, or *Camphyl Alcohol* $C_{10}H_{18}O$, is found in the old trunks of *Dryobalanops Camphora*, a tree growing in Borneo, Java, and Sumatra, and has been obtained by the action of sodium on common camphor (page 303), and, together with campholic acid, by heating camphor with an alcoholic potash solution.

Borneol forms small transparent crystals, smelling like common camphor and pepper. It melts at 198°, and boils at 212°. Nitric acid converts it into common camphor.

Borneol is a monad alcohol; on heating it with hydrochloric acid, *camphyl chloride* $C_{10}H_{17}Cl$ is formed, a body resembling solid terpene monohydrochloride.

Camphyl-methyl Ether $\left.\begin{matrix}CH_3\\C_{10}H_{17}\end{matrix}\right\}O$.—The formation of this compound from common camphor has already been described; it is a liquid smelling like camphor, and boiling at 194°·5.

Camphyl Acetate $\left.\begin{matrix}C_{10}H_{17}\\C_2H_3O\end{matrix}\right\}O$ is obtained by the action of acetic anhydride upon sodium camphylate; it is a colourless liquid, boiling at 230°, and possessing a camphor-like odour.

When borneol is heated with phosphorus pentoxide, it is resolved in water, and *Borneene* $C_{10}H_{16}$, a liquid occurring also in the volatile oil of *Laurus Camphora* and oil of valerian. By leaving it in contact with potash solution, it is converted again into borneol.

Levo-borneol is found in the fusel oil of spirits from madder-root; it possesses all the properties of borneol, with the exception that it has a levo-rotatory power, whilst borneol turns the plane of polarization to the right.

Geraniol, or *Geranyl Alcohol* $C_{10}H_{18}O$, is found in *Indian geranium oil*. It is a strongly refractive liquid, boiling at 232°, and possessing a very agreeable smell, like roses. It is optically inactive, and yields on oxidation valerianic acid.

Geranyl Chloride $C_{10}H_{17}Cl$ is obtained by heating geraniol with hydrochloric acid. It is a yellowish liquid, with an aromatic smell. By acting on it with the potassium salts of valerianic, benzoic or cinnamic acids, the geranyl-ethers of these acids have been produced. They are oily liquids, possessing an aromatic odour.

Digeranyl Ether $\left.\begin{matrix}C_{10}H_{17}\\C_{10}H_{17}\end{matrix}\right\}O$, a liquid boiling at about 190°, and smelling like peppermint, is formed by heating geraniol with geranyl chloride.

Geranyl Sulphide $\left.\begin{matrix}C_{10}H_{17}\\C_{10}H_{17}\end{matrix}\right\}S$ is obtained by acting with geranyl chloride on an alcoholic solution of potassium sulphide; it is a yellow liquid, possessing a very disagreeable smell.

When geraniol is heated with zinc chloride or with phosphorus pentoxide, it is resolved into water and *Geranicne* $C_{10}H_{16}$, a limpid, mobile liquid, boiling at 163°, and smelling like carrots.

Other isomerides of borneol exist in the oil of cajeput, and of coriander.

Menthol, or *Menthyl Alcohol* $C_{10}H_{20}O$, occurs in the oil of peppermint. It forms colourless prismatic crystals, smelling strongly like the plant. It melts at 36°, and boils at 210°.

Menthyl Chloride $C_{10}H_{19}Cl$ is a liquid formed by heating menthol with hydrochloric acid.

When menthol is heated with phosphorus pentoxide, *Menthene* $C_{10}H_{18}$ is produced, a liquid boiling at 163°.

Eucalyptol $C_{12}H_{20}O$ is contained in the leaves of *Eucalyptus globulus*, a tree growing in Tasmania. It is a colourless liquid, boiling at 175°, and possessing an aromatic smell. By distilling it with phosphorus pentoxide, it is decomposed into water, and *Eucalyptene* $C_{12}H_{18}$, a liquid boiling at 165°.

Patchouli Oil.—This substance is a mixture of two isomeric substances having the composition $C_{15}H_{26}O$. One of them, called *patchouli-camphor*, crystallizes from the oil on standing in hexagonal prisms, melting at 55°, and boiling at 296°. On distilling it, or the liquid portion of the oil, with zinc chloride, *Patchoulene* $C_{15}H_{26}$, a liquid boiling at 250°, is formed.

OXIDATION-PRODUCTS OF CAMPHORS.

Campholic Acid $C_{10}H_{18}O_2$.—This monobasic acid is formed by heating camphor with potash-lime to 400°, and, together with borneol, when potassium is added to a solution of petroleum, at 130°. It is but sparingly soluble in water; from alcohol it crystallizes in prisms melting at 95°, and volatilizing without decomposition. When campholic acid is heated with phosphorus pentoxide, or when a campholate is subjected to dry distillation, *campholene* C_9H_{16} is produced, a liquid boiling at 130°.

Dextrocamphoric Acid $C_8H_{14}\left\{\begin{matrix}CO.OH\\CO.OH\end{matrix}\right.$ is produced by the action of boiling nitric acid on camphor or campholic acid. It is sparingly soluble in cold water, more freely in boiling water, and forms scaly crystals, having a faint acid taste, and melting at 175°. On distillation, it splits up into water, and *camphoric anhydride* $C_8H_{14}\left\{\begin{matrix}CO\\CO\end{matrix}\right\}O$, which sublimes in long, brilliant needles, melting at 217°. When camphoric acid is fused with potash, it yields volatile fatty acids and *pimelic acid* $C_7H_{12}O_4$ (see page 236).

Calcium Camphorate $C_8H_{14}(CO_2)_2Ca + 8H_2O$ is readily soluble in water, and forms large crystals. When it is heated it is resolved into calcium carbonate and *phorone* $C_9H_{14}O$, a liquid boiling at 208°, and yielding, by treatment with chromic acid-solution, carbon dioxide, acetic acid, and *adipic acid* $C_6H_{10}O_4$ (see page 235).

Levocamphoric acid has been obtained from the camphor of *Pyrethrum Parthenium*; it differs from common camphoric acid by having a left-handed polarization; both active acids combine, forming an inactive acid, corresponding to racemic acid.

Camphoronic Acid $C_7H_{10}O\left\{\begin{matrix}CO.OH\\CO.OH\end{matrix}\right.$ is an oxidation-product of camphoric acid, and may be isolated from the mother liquors obtained in the preparation of the latter compound. It is readily soluble in water, crystallizing, with one molecule of water, in small needles or shining prisms, possessing a rancid and strongly sour taste. The anhydrous acid melts at 115°, and distils at a higher temperature without decomposition. Although a bibasic acid, it forms also salts containing three equivalents of a metal, resembling in that respect deoxalic acid (page 240).

Oxycamphoronic Acid $C_7H_{10}O_2\left\{\begin{matrix}CO.OH\\CO.OH\end{matrix}\right.$ is obtained by heating crystallized camphoronic acid with bromine in sealed tubes to 130°:—

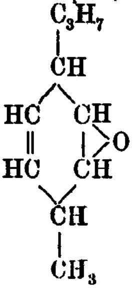
$$C_9H_{12}O_5 + H_2O + Br_2 = C_9H_{12}O_6 + 2HBr$$

It is freely soluble in water, and crystallizes on slowly evaporating the solution in splendid monoclinic prisms, containing one molecule of water. The anhydrous acid melts at 210°, and may be distilled without decomposition.

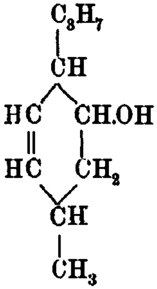
On fusing camphoronic or oxycamphoronic acid with caustic potash, butyric acid and carbon dioxide are produced.

Camphor and its derivatives are nearly allied to the aromatic compounds; for, by simply abstracting the elements of water from camphor, we obtain *cymene* or *methyl-isopropyl benzene* (page 301.). The constitution of camphor and some of its derivatives can be explained by assuming the following formulæ:—

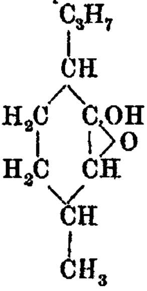
Camphor.



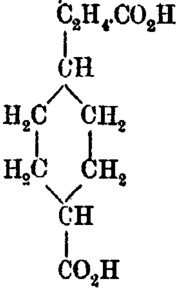
Borneol.



Campholic Acid.



Camphoric Acid.



RESINS.

The terpenes, when exposed to the air, undergo gradually oxidation, become more and more viscid, and exhibit an acid reaction; and at last are converted into a brittle, amorphous substance. Such products are found in nature, either mixed with non-oxidized hydrocarbons, being called *balsams*, whilst the solid and brittle products of oxidation of the terpenes are called *resins*.

The resins are mixtures of weak acids; they dissolve in alkalis, forming a kind of soap.

Common Resin, or *Colophony*, is left behind by distilling turpentine with water. By exhausting it with cold alcohol, *sylvic acid* $C_{20}H_{30}O_2$ goes in solution, which on evaporation crystallizes in flat needles, melting at 129°, and solidifying to an amorphous mass. It is a monobasic acid, forming soluble and crystallized salts with the alkali-metals, whilst those of the other metals are insoluble. Besides sylvic acid, colophony contains the isomeric but amorphous *pinic acid.*

A third isomeride, called pimaric acid, exists in galipot, the resin of *Pinus maritima.* It forms crystals melting at 149°, and is converted into sylvic acid by distilling it *in vacuo.*

Copaibic Acid $C_{20}H_{30}O_2$ occurs together with a diterpene $C_{20}H_{32}$ and sylvic acid in copaiba balsam; it crystallizes from alcohol in transparent prisms.

Guaiaretic Acid $C_{20}H_{26}O_4$ is a chief constituent of guaiacum, and crystallizes in colourless brittle needles, melting at 77°. Besides this compound, guaiacum contains other resinous substances, and *guaiacic acid* $C_6H_8O_3$, which is soluble in water, and sublimes on heating. When a solution of guaiacum in presence of an alkali is acted upon by ozone, nitrous fumes, chromic acid, ferric chloride, chlorine, and other oxidizing agents, it assumes a fine blue colour.

When guaiacum is subjected to dry distillation, it yields *guaiacc* C_5H_8O, a liquid smelling like bitter almonds, and *guaiacol* and *creosol*, compounds belonging to the aromatic group.

Amber.—This fossil resin occurs on the shores of the Baltic, either in the sea or in the sand, and has also been found together with lignite or brown-coal. It is an amorphous, brittle mass, having a yellowish or brown colour; on heating, it melts at about 280°, giving off an aromatic vapour. It contains free succinic acid, a resin soluble in alcohol, and amber-bitumen, a substance insoluble in all solvents.

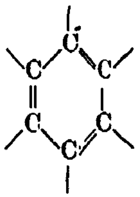
Besides these resins, there exist a great many more, most of which are used for making varnishes and for other purposes; but they have been very little examined. Many of them contain aromatic compounds, or yield such on fusion with caustic potash. These will be mentioned again when these bodies are described.

AROMATIC COMPOUNDS.

This large group has obtained its name from the fact that many of its members occur in essential oils, balsams, gum-resins, and similar bodies, possessing an aromatic odour.

All aromatic compounds contain at least six atoms of carbon; they contain a common nucleus, in which the six carbon atoms are linked together in such a way that six combining units remain unsaturated.

The carbon atoms forming the aromatic nucleus are united together by one and two combining units alternately, thus:—

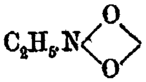


The most simple aromatic hydrocarbon is *benzene* C_6H_6, and all other compounds belonging to the group are derived from it by replacing hydrogen by other elements or radicals.

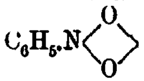
When one atom of hydrogen is replaced by chlorine, we obtain *chlorobenzene* C_6H_5Cl (formerly called *phenyl chloride*[1]) a body differing from the chlorides of the alcohol radical by being a much more stable compound, and not undergoing double decomposition with silver salts, hot alcoholic potash, or ammonia. Other aromatic compounds containing chlorine, or other halogen-elements combined with the aromatic nucleus, show a similar behaviour; the chlorine, &c., being much more firmly combined with the carbon than in the haloid compounds of other radicals.

The action of concentrated nitric acid on aromatic compounds is very characteristic; they are converted into *nitro-compounds*, such as *nitrobenzene* $C_6H_4.NO_2$, *nitrochlorobenzene* $C_6H_4Cl.NO_2$, &c. Reducing agents convert these nitro-compounds into *amido-compounds*; thus nitrobenzene yields with nascent hydrogen, *amidobenzene* or *aniline* $C_6H_5.NH_2$; the constitution of these nitro-compounds is, therefore, similar to that of *nitro-ethane* $C_2H_5.NO_2$ (see page 113).

Nitro-ethane.



Nitrobenzene.

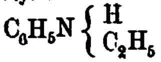


Ethylamine.
$C_2H_5.NH_2$

Aniline.
$C_6H_5.NH_2$

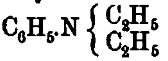
The aromatic amido-compounds combine with acids like the amines, and are acted upon by the iodides of the alcohol radicals like the latter, forming compounds such as:—

Ethyl-amidobenzene.



$$C_6H_5N\begin{cases}H\\C_2H_5\end{cases}$$

Diethyl-amidobenzene.



$$C_6H_5.N\begin{cases}C_2H_5\\C_2H_5\end{cases}$$

The latter compound combines with ethyl iodide, forming *phenyl-triethylammonium iodide* $N[C_6H_5(C_2H_5)_3]$, a crystallized salt, which, when acted upon by silver oxide and water, yields the corresponding strongly alkaline and caustic hydroxide.

---

[1] *Phenyl* is the name given to the monad group C_6H_5.

Whilst in these reactions the amido-compounds show the greatest resemblance to the compound ammonias, they differ from the latter in several respects; thus they have no alkaline reaction, and no ammoniacal smell.

Concentrated sulphuric acid acts on aromatic bodies in a similar way to nitric acid; one atom of hydrogen combined with the aromatic nucleus being replaced by the monad group $SO_2.OH$, a *sulpho-acid* is formed; benzene yielding *benzenesulphonic acid* $C_6H_5.SO_2.OH$.

When this acid is fused with potash, the group SO_3H is replaced by hydroxyl, and *phenol* is formed:—

$$C_6H_5.SO_3K + KOH = SO_3K_2 + C_6H_5.OH$$

The *phenols* were formerly regarded as alcohols, but they differ from the latter compounds in many respects. By oxidizing agents they are not very readily attacked, and yield neither aldehydes nor ketones or acids. They have the character of weak acids; the hydrogen of the hydroxyl being much more readily replaced by a metal than this is the case in the true alcohols.

Thus ethyl alcohol is not acted upon by potash, which with phenol readily forms water, and *potassium phenate* $C_6H_5.OK$.

Another characteristic difference between alcohols and phenols is found in the action of concentrated acids. Hydrochloric acid and alcohol yield ethyl chloride, but phenol is not acted upon by this acid at all. Whilst alcohol is converted by strong nitric acid into ethyl nitrate, and by sulphuric acid into ethyl sulphuric acid, the phenols yield substitution-products, such as *nitrophenol* $C_6H_4(NO_2)OH$, and *phenolsulphonic* acid $C_6H_4\left\{\begin{matrix}SO_3H\\OH\end{matrix}\right.$;—

$$C_2H_5.OH + SO_2\left\{\begin{matrix}OH\\OH\end{matrix}\right. = SO_2\left\{\begin{matrix}OH\\OC_2H_5\end{matrix}\right. + H_2O$$

$$C_6H_5.OH + SO_2\left\{\begin{matrix}OH\\OH\end{matrix}\right. = SO_2\left\{\begin{matrix}OH\\C_6H_4.OH\end{matrix}\right. + H_2O$$

The phenols are easily reduced again to the corresponding hydrocarbons by passing their vapour over red-hot zinc-dust:—

$$C_6H_5.OH + Zn = C_6H_6 + ZnO$$

When amines or amides are acted upon by nitrous acid, the group NH_2 is replaced by OH; by the same reaction, aromatic amido-compounds may be converted into phenols; the reaction, however, takes place in two stages. Thus, by treating aniline nitrate with nitrous acid, *Diazobenzene nitrate* is formed:—

$$C_6H_5.NH_2.HNO_3 + HNO_2 = C_6H_5N_2.NO_3 + 2H_2O$$

These diazo-compounds are very unstable bodies, and the different transformations which they undergo are of great interest, as by means of them a very great number of derivatives can be obtained. Thus, on boiling a diazo-compound with water, a phenol is formed:—

$$C_6H_5N_2.NO_3 + H_2O = C_6H_5.OH + N_2 + HNO_3$$

By using absolute alcohol instead of water, the group N_2 is replaced by hydrogen, the alcohol being oxidized to aldehyde; thus, on treating the acid sulphate of diazobenzene in this way, we obtain benzene:—

$$C_6H_5N_2.SO_4H + C_2H_6O = C_6H_6 + SO_4H_2 + C_2H_4O$$

By acting on a diazo-compound with strong acids, the latter take part in the reaction; by treating diazobenzene nitrate with nitric acid, different nitrophenols are formed, whilst hydriodic acid converts it into *iodobenzene*:—

$$C_6H_5.N_2.NO_3 + HI = C_6H_5I + N_2 + HNO_3$$

The diazo-compounds contain the dyad group N_2, the two nitrogen-atoms being linked together by two combining units of each; diazobenzene is therefore a monad radical, having the following constitution:—

$$—N=N—C_6H_5$$

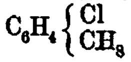
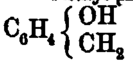
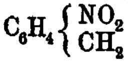
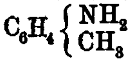
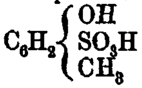
By the action of oxidizing agents on amido-compounds, or by that of weak reducing agents upon nitro-compounds, a class of bodies is obtained called *azo-compounds*, in which two aromatic nuclei are linked together by nitrogen:—

$$\begin{array}{c}\text{Amidobenzene.}\\ C_6H_5.NH_2\\ \\ C_6H_5.NH_2\end{array} + O_2 = \begin{array}{c}\text{Azobenzene.}\\ C_6H_5.N\\ \|\\ C_6H_5.N\end{array} + 2H_2O$$

The aromatic compounds, containing more than six atoms of carbon, are formed by replacing hydrogen in benzene or its substitution-products by organic radicals. Thus the most simple homologue of benzene is *Methyl-benzene* or *Toluene* $C_6H_5.CH_3$, a hydrocarbon which in its chemical properties exhibits a close analogy to benzene, yielding readily substitution-products with chlorine, nitric acid, sulphuric acid, &c. These compounds have the greatest analogy with the benzene derivatives when the substitutions have taken place in the aromatic nucleus. But the hydrogen of the methyl can also be replaced by other elements and radicals; and thus compounds are formed, which have the closest resemblance in their chemical properties with the derivatives of marsh-gas. By replacing one atom of hydrogen in the methyl of toluene, a series of compounds is obtained containing the alcohol-radical *Benzyl*:—

TOLUENE, METHYL-BENZENE OR PHENYL-METHANE.

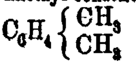
$C_6H_5.CH_3$.

Monochlorotoluene.  $C_6H_4\left\{\begin{matrix}Cl\\CH_3\end{matrix}\right.$	Benzyl Chloride. $C_6H_5.CH_2Cl$
Cresol or Methyl-phenol.  $C_6H_4\left\{\begin{matrix}OH\\CH_2\end{matrix}\right.$	Benzyl Alcohol. $C_6H_5.CH_2.OH$
Nitrotoluene.  $C_6H_4\left\{\begin{matrix}NO_2\\CH_2\end{matrix}\right.$	Benzyl Nitrite. $C_6H_5.CH_2.NO_2$
Amidotoluene.  $C_6H_4\left\{\begin{matrix}NH_2\\CH_3\end{matrix}\right.$	Benzylamine. $C_6H_5.CH_2.NH_2$
Cresolsulphonic Acid.  $C_6H_3\left\{\begin{matrix}OH\\SO_3H\\CH_3\end{matrix}\right.$	Benzylsulphuric Acid. $C_6H_5.CH_2.SO_4H$
	Benzaldehyde. $C_6H_5.COH$
	Benzoic Acid. $C_6H_5.CO.OH$

The number of aromatic compounds is very large, and amongs them a great number of isomerides occur. Thus we have th following isomeric hydrocarbons:—

C_8H_{10}

Dimethyl-benzene.



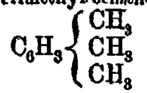
$C_6H_4\left\{\begin{matrix}CH_3\\CH_3\end{matrix}\right.$

Ethyl-benzene.

$C_6H_5.C_2H_5$

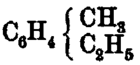
C_9H_{12}

Trimethyl-benzene.



$C_6H_3\left\{\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\right.$

Methyl-ethyl-benzene.



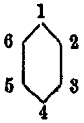
$C_6H_4\left\{\begin{matrix}CH_3\\C_2H_5\end{matrix}\right.$

Propyl-benzene.

$C_6H_5.C_3H_7$

But these formulæ do not exhaust the number of isomerides, as isomerism in the aromatic group can also be caused by the differen relative positions of elements or radicals combined with the nucleus. Thus we find that dimethyl-benzene exists in three different forms, the cause of it being the different positions of the two methyls.

If we represent the aromatic nucleus as an hexagon, and number the corners where the carbon-atoms are supposed to be, we see at once that three isomeric dimethyl-benzenes may exist:—



The methyl groups having the following positions:—

1 : 2
1 : 3
1 : 4

No further different positions of the two methyls are possible, for 1 : 5 = 1 : 3 and 1 : 6 = 1 : 2.

The hydrocarbon C_9H_{12}, which we have represented in three isomeric forms, can exist in eight different modifications. There are, first of all, three trimethyl-benzenes:—

1 : 2 : 3
1 : 2 : 4
1 : 2 : 5

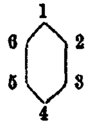
Further, there can exist three methyl-ethyl-benzenes and two propyl-benzenes, one containing normal propyl, and the other isopropyl.

As the isomeric aromatic hydrocarbons have generally a great resemblance in their physical properties, it is of the greatest importance to have means for distinguishing them from each other. This can easily be done by studying their products of oxidations.

By heating an aromatic hydrocarbon with very dilute nitric acid, one of the alcohol radicals is first oxidized to carboxyl; methyl-benzene, ethyl-benzene, amyl-benzene, &c., yielding *benzoic acid*. The formation of this acid, therefore, proves the existence of only one alcohol radical in an aromatic hydrocarbon.

The three methyl-benzenes as well as ethyl-methyl-benzene yield isomeric *methyl-benzoic acids* $C_6H_4\left\{\begin{matrix}CH_3\\CO.OH\end{matrix}\right.$, and diethyl-benzene yields as first product of oxidation, *ethyl-benzoic acid* $C_6H_4\left\{\begin{matrix}C_2H_5\\CO.OH\end{matrix}\right.$. Besides these monobasic acids, there is, at the same time, a bibasic acid $C_6H_4\left\{\begin{matrix}CO.OH\\CO.OH\end{matrix}\right.$ formed, which is obtained in larger quantity by using stronger oxidizing agents, such as a solution of potassium dichromate in dilute sulphuric acid. This bibasic acid exists of course, also, in three isomeric modifications, differing from each other by their physical properties, as well as those of their salts. In the same way, a hydrocarbon containing three alcohol-radicals will yield by successive oxidation a monobasic, a bibasic, and a tribasic acid, one alcohol-radical after the other being oxidized to carboxyl.

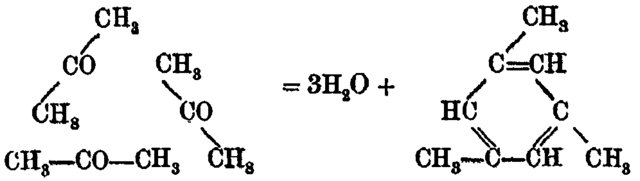
But we are not only able thus to fix the number of the alcohol-radicals, but in many cases we are in a position to determine the relative positions of these radicals, as well as that of other groups replacing hydrogen in benzene, as the following examples will show:—



	1, 2.	1, 3.	1, 4.
$C_6H_4\left\{\begin{matrix}OH\\OH\end{matrix}\right.$	Hydroquinone.	Pyrocatechin.	Resorcin.
$C_6H_4\left\{\begin{matrix}I\\OH\end{matrix}\right.$	Ortho-iodophenol.	Meta-iodophenol.	Para-oidophenol.
$C_6H_4\left\{\begin{matrix}OH\\CO.OH\end{matrix}\right.$	Salicylic Acid.	Oxybenzoic Acid.	Paraoxybenzoic Acid.
$C_6H_4\left\{\begin{matrix}CH_3\\CH_3\end{matrix}\right.$	Orthoxylene.	Isoxylene.	Methyl-toluene.
$C_6H_4\left\{\begin{matrix}CO.OH\\CO.OH\end{matrix}\right.$	Phthalic Acid.	Isophthalic Acid.	Terephthalic Acid.

In phthalic acid, the two carboxyls occupy the positions 1, 2. This we know from the fact that this acid is obtained by the oxidation of naphthalene $C_{10}H_8$, a hydrocarbon of known constitution, and in which, as will be shown further on, two carbon-atoms are linked to two adjoining atoms of the aromatic nucleus.

Isophthalic acid, belonging to the series 1, 3, is obtained by oxidizing isoxylene; this hydrocarbon has been prepared from mesitylene or trimethyl-benzene, in which the three methyls have the symmetrical positions 1, 3, 5. This follows from the formation of mesitylene, which is obtained by heating acetone with sulphuric acid (page 153), three molecules losing three molecules of water, and the residues joining together thus:—



On oxidizing mesitylene, we obtain monobasic mesitylenic acid $C_6H_3\left\{\begin{matrix}CO.OH\\CH_3\\CH_3\end{matrix}\right.$ which, when heated with quicklime, is resolved into carbon dioxide and isoxylene. From this it follows that in isoxylene, as well as in isophthalic acid, the two radicals have the positions 1, 3 (= 1, 5 or 3, 5).

Isophthalic acid is also produced by heating a mixture of the potassium salts of formic acid and sulphobenzoic acid :—

$$C_6H_4\left\{\begin{matrix}SO_3K\\CO_2K\end{matrix}\right. + CO_2KH = C_6H_4\left\{\begin{matrix}CO_2K\\CO_2K\end{matrix}\right. + SO_3KH$$

Now, as on fusing sulphobenzoic acid with potash we obtain oxybenzoic acid, it is obvious that the latter is also a member of the second series.

We know now the constitution of phthalic acid and isophthalic acid, and therefore also that of terephthalic acid, in which the carboxyls occupy the positions 1, 4; and as methyl-toluene yields on oxidation terephthalic acid, the methyl-groups in this hydrocarbon have the same position.

Methyl-toluene is obtained from parabrometoluene, which on oxidation yields parabromobenzoic acid; and on fusing the latter compound with caustic potash, it is converted into para-oxybenzoic acid.

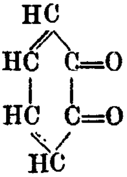
When the potassium salt of benzenedisulphonic acid is heated with potassium cyanide, the nitrile of terephthalic acid is produced; and by fusing benzenedisulphonic acid with caustic potash, resorcin is formed; the latter compound is also obtained by the action of caustic potash on para-iodophenol.

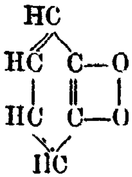
Thus the constitution of all the members of the fourth series is perfectly made out, and consequently, also, that of orthoxylene and of salicylic acid; moreover, the latter acid readily splits up into water and salicylic anhydride $C_6H_4\left\{\begin{matrix}CO\\O\end{matrix}\right.>$ whilst its isomerides are much more stable; and from this it also appears very probable that the two side-chains of salicylic acid are as near together as possible.

Hydroquinone differs from its isomerides by readily losing two atoms of hydrogen, when treated with oxidizing agents, and yielding quinone $C_6H_4O_2$, which by nascent hydrogen is very easily reconverted into hydroquinone.

The constitution of quinone may be expressed by one of the following formulæ :—

$$CO{=}CH{-}CH{-}CH{-}CH{-}CO$$





The first formula is very improbable, for we cannot assume that the closed chain of carbon-atoms would be so readily broken by oxidation and closed again by reduction. The second formula has also to be rejected, because a compound having this constitution would, with nascent hydrogen, yield $C_6H_2(OH)_2$, just as acetone gives secondary propyl alcohol. Moreover, when tetrachloroquinone $C_6Cl_4O_2$ is treated with phosphorus pentachloride, it is not converted into C_6Cl_8, which compound would have been found if quinone contained the oxygen combined, as shown in the second formula; but the product consists of hexachlorobenzene C_6Cl_6. Quinone must therefore contain the dyad group $\begin{matrix}O\diagdown\\O\diagup\end{matrix}\!\!>$. Now, as the two isomerides of hydroquinone do not yield by oxidation a quinone, the oxygen-atoms must occupy such a position that they can easily combine with each other; and this will most readily take place if they are close together as possible, or occupy the positions 1, 2. Hydroquinone is obtained by fusing ortho-iodophenol with caustic potash, and consequently this body belongs to the first group, and meta-iodophenol and pyrocatechin to the series 1, 3.

Although the aromatic hydrocarbons and their substitution-products behave in most of their reactions like saturated compounds, yet under certain conditions they can be made to combine directly with other elements, like the olefines and other non-saturated compounds.

These additive products still contain a closed chain of six carbon-atoms; the connection between them become only loosened. From this it follows that no more than six monad groups can be added to an aromatic compound,[1] and experience has proved the truth of this conclusion. Thus benzene can combine with one, two, or three molecules of chlorine, or three molecules of hypochlorous acid, forming the following compounds:—

Benzene Dichloride	$C_6H_6Cl_2$
Benzene Tetrachloride	$C_6H_6Cl_4$
Benzene Hexachloride	$C_6H_6Cl_6$
Benzene Trichlorhydrate	$C_6H_6Cl_3(OH)_3$

These compounds are much less stable than the products of substitution, and are again readily converted into compounds in which the carbon-atoms are linked together in the same manner as in benzene itself.

Thus, on treating the hexachloride with an alcoholic potash-solution it is resolved into three molecules of hydrochloric acid and one of trichloro-benzene. In these reactions benzene behaves exactly like ethene, which combines with chlorine to ethene dichloride—a body in which the two carbon-atoms are linked together by one combining unit of each. By the action of alcoholic potash, hydrochloric acid is taken out, and chlorethene C_2H_3Cl is formed, in which the carbon-atoms are again linked together, as in ethene.

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[1] Excepting, of course, those aromatic compounds which contain non-saturated radicals as side-chains.

Hydrogen can also combine with aromatic hydrocarbons, but only with those containing alcohol-radicals. The number of atoms of hydrogen combining with the hydrocarbon appears to depend, not only on the number of these radicals, but also on the relative positions.

To obtain these additive products, the hydrocarbon is heated in sealed tubes with phosphonium iodide (a compound of hydriodic acid with hydrogen phosphide). The hydriodic acid is the reducing agent, being decomposed into hydrogen and iodine, which latter is immediately acted upon by the hydrogen phosphide, and again converted into hydriodic acid; this change going on until at last only phosphorus iodide and red phosphorus are left behind.

By subjecting benzene to this reaction, it is not changed even at 350°. Methyl-benzene combines with two atoms of hydrogen, and forms the hydrocarbon $C_6H_7.CH_3$. Dimethyl-benzene takes up four atoms of hydrogen, yielding $C_6H_8\left\{\begin{array}{l}CH_3\\CH_3\end{array}\right.$, and trimethyl-benzene combines with six atoms of hydrogen, forming the compound $C_6H_9\left\{\begin{array}{l}CH_3\\CH_3\\CH_3\end{array}\right.$.

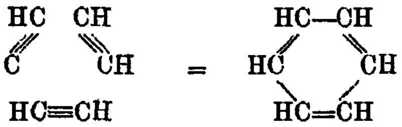
There exist also aromatic acids which will combine with hydrogen in the nascent state.

COMPOUNDS WITH SIX ATOMS OF CARBON.

BENZENE C_6H_6.

Benzene, or *Benzol*, is a colourless, strongly refractive, and mobile liquid, boiling at 81°, and solidifying at 0°, to colourless crystals. It has a density of 0·899 at 0°, and of 0·878 at 20°, and a peculiar aromatic odour. It is very inflammable, burning with a very luminous and very smoky flame. It is almost insoluble in water, but dissolves freely in alcohol and ether. It dissolves iodine, sulphur, phosphorus, fats, resins, and many other compounds, which are insoluble or only sparingly soluble in water and alcohol; and hence it is used for preparing or purifying many compounds.

Benzene has been produced artificially from its elements. When acetylene, which, as we have seen (page 274), may be formed by the direct combination of carbon with hydrogen, is heated in a long, narrow, bent bell-jar to a temperature at which the glass begins to soften, it is converted into polymeric modifications, the principal of which is *Tri-acetylene* or *Benzene*:—



Benzene is also formed in the dry distillation of many organic substances, and is contained in considerable quantity in coal-naphtha (the more volatile portion of coal-tar), from which it is now almost always prepared. The oil, after treatment with sulphuric acid and caustic soda, is submitted to fractional distillation, and the portion distilling after a few distillations between 80° to 85° collected apart. This distillate consists principally of benzene, but contains yet small quantities of paraffins, olefines, and acetylene-hydrocarbons. On cooling it down to 12°, the benzene solidifies, and is purified from the adhering liquid by strong pressure. By repeating this process, an almost pure benzene is prepared. It is now manufactured in large quantity for the preparation of aniline, but the commercial product always contains other hydrocarbons in a smaller or larger quantity.

A very pure benzene may be prepared by the distillation of a mixture of one part of benzoic acid with three parts of slaked lime:—

$$C_6H_5.CO_2H + CaO = C_6H_6 + CaCO_3$$

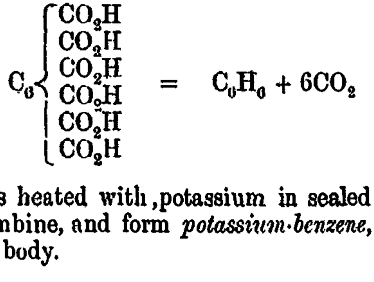
a reaction corresponding to the preparation of marsh-gas from acetic acid.

All other aromatic acids which are derived, like benzoic acid, from benzene, by hydrogen being replaced by carboxyl, are decomposed in a similar way by heating them with lime:—

Phthalic Acid.

$$C_6H_4\left\{\begin{array}{l}CO_2H\\CO_2H\end{array}\right. = C_6H_6 + 2CO_2$$

Mellitic Acid.



$$C_6\left\{\begin{array}{l}CO_2H\\CO_2H\\CO_2H\\CO_2H\\CO_2H\\CO_2H\end{array}\right. = C_6H_6 + 6CO_2$$

When benzene is heated with potassium in sealed tubes to 250°, the two bodies combine, and form *potassium-benzene*, a bluish black and very explosive body.

SUBSTITUTION-PRODUCTS OF BENZENE.

Monochlorobenzene C_6H_5Cl.—To obtain chlorine substitution-products, chlorine is passed into benzene in presence of a little iodine, the first product being monochlorobenzene, a colourless liquid, smelling like bitter almonds, and boiling at 138°. The same substance is produced by the action of phosphorus pentachloride upon phenol.

Monochlorobenzene is not acted upon by heating it with silver salts or alcoholic solutions of potash, ammonia, and potassium acetate. When treated with sodium-amalgam, it is reconverted into benzene.

By the further action of chlorine upon benzene, the following bodies have been obtained; they are all white crystalline solids:—

Dichlorobenzene . . .	$C_6H_4Cl_2$	53°	171°
Trichlorobenzene . .	$C_6H_3Cl_3$	17	206
Tetrachlorobenzene .	$C_6H_2Cl_4$	139	240
Pentachlorobenzene .	C_6HCl_5	74	272
Hexachlorobenzene .	C_6Cl_6	226	326

Hexchlorobenzene is also formed when the vapour of chloroform $CHCl_3$, or tetrachlorethene CCl_4, is passed through red-hot tubes.

Monobromobenzene C_6H_5Br is slowly formed by mixing bromine with benzene, and exposing the mixture to the daylight. It is a liquid resembling chlorobenzene, and boiling at 154°.

Dibromobenzene $C_6H_4Br_2$.—When benzene is heated with six times its weight of bromine, it yields two isomeric bibromobenzenes, which may be separated by fractional distillation.

Paradibromobenzene crystallizes in large colourless prisms, melting at 89°, and boiling at 219°.

Orthodibromobenzene is a liquid boiling at 213°, and solidifying at a low temperature to crystals, melting at − 1°.

Metadibromobenzene has been produced by converting aniline into dibromo-aniline, and acting on this compound with an alcoholic solution of nitrous acid. Metadibromobenzene is a colourless liquid, boiling at 215°, and not solidifying even at − 28°.

When benzene is heated with an excess of bromine, the higher substitution-products are formed, which are colourless, crystalline solids.

Moniodobenzene C_6H_5I.—Iodine alone does not act upon benzene, even at a high temperature; but in presence of iodic acid, substitution-products are formed. The iodic acid acts as oxidizing agent, taking hydrogen away, in which place iodine enters. At the same time, a considerable quantity of carbon dioxide is formed, a part of the benzene being destroyed by oxidation. Momiodobenzene is a colourless liquid, which assumes a reddish colour on exposure to the light. It boils at 185°, and is as stable a compound as chlorobenzene.

The most convenient method to prepare this compound in quantity consists in the decomposition of a salt of diazobenzene with hydriodic acid. Substitution-products of benzene are also produced by treating silver benzoate with iodine chloride :—

$$C_6H_5.CO_2Ag + ICl = C_6H_5I + AgCl + CO_2$$

Monofluobenzene C_6H_5F, is produced by distilling fluobenzoic acid with quicklime. It is a scaly, crystalline mass, melting at 40°, and boiling at 180°. Its odour resembles that of benzene.

Nitrobenzene $C_6H_5NO_2$.—Benzene dissolves in concentrated nitric acid with the evolution of heat; on the addition of water, nitrobenzene is precipitated as a heavy oily liquid :—

$$C_6H_2 + NO_2.OH = C_6H_5NO_2 + H_2O$$

Nitrobenzene has generally a brown colour, but when quite pure it is a pale yellow, strongly refractive liquid, boiling at 220°. It has a burning sweet taste, and a smell resembling that of oil of bitter almonds, and of cinnamon.

Dinitrobenzene $C_6H_4(NO_2)_2$ is formed by boiling nitrobenzene with strong nitric acid, or by acting upon benzene with a mixture of concentrated sulphuric and nitric acids. It crystallizes from nitric acid or from alcohol in long, glistening, colourless needles, melting at 86°.

When mono- or dinitrobenzene, or other nitro-compounds are heated with potash, they are decomposed, yielding potassium cyanide, and other products which have not been examined.

By the action of strong nitric acid upon the substitution-products of benzene, already described, nitro-compounds of the latter are obtained.

Benzenesulphonic Acid $C_6H_5.SO_2.OH$.—When benzene is shaken with concentrated sulphuric acid, it is dissolved :—

$$C_6H_6 + SO_2\left\{\begin{matrix}OH\\OH\end{matrix}\right. = C_6H_5.SO_2.OH + H_2O$$

On neutralizing the diluted solution with carbonate of barium or lead, the excess of sulphuric acid is removed, and the solution contains the benzenesulphonates of these metals. To obtain the free acid, the salts are decomposed either by sulphuric acid or hydrogen sulphide, and the filtered solution is evaporated. Benzenesulphonic acid forms small colourless deliquescent plates.

Benzenesulphonic Chloride $C_6H_5.SO_2Cl$ is obtained by the action of phosphorus pentachloride upon sodium benzenesulphonate; it is an oily liquid boiling at 246°, which is decomposed by boiling water. By the action of ammonia it is converted into *Benzenesulphonamide* $C_6H_5.SO_2.NH_2$, a colourless crystalline solid.

Benzenedisulphonic Acid $C_6H_4\left\{\begin{matrix}SO_3.OH\\SO_2OH\end{matrix}\right.$ is produced by heating the monosulphonic acid with fuming sulphuric acid. It forms a crystalline deliquescent mass. The barium-salt is very soluble in water, but the lead-salt less so.

Benzene Sulphoxide or Sulphobenzide $\left.\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\right\}SO_2$.—To obtain this compound, benzene is gradually added to sulphur trioxide. It is a solid, sparingly soluble in water, and crystallizing from alcohol in rhombic plates.

Benzenesulphonic Acid $C_6H_5.SO.OH$.—The sodium-salt of this acid is produced by the action of sodium amalgam on an etherial solution of benzenesulphonic chloride. The free acid is sparingly soluble in cold water, and crystallizes from a boiling solution in large brilliant prisms. It is readily oxidized even by the oxygen of the air, and converted into benzenesulphonic acid.

Substitution-products of benzenesulphonic acid are produced by the action of sulphuric acid on the substituted benzenes.

Phosphenyl Chloride $C_6H_5.PCl_2$ is formed by passing a gaseous mixture of benzene and phosphorus trichloride repeatedly through a tube heated nearly to redness. It is a very refractive liquid, boiling at 222°, possessing a strong pungent smell, and fuming in the air.

AMIDOBENZENE, OR ANILINE, $C_6H_5.NH_2$.

By the action of reducing agents, nitrobenzene is converted into amidobenzene:—

$$C_6H_5.NO_2 + 3H_2 = C_6H_5.NH_2 + 2H_2O$$

To effect this reduction on the small scale, nitrobenzene is gently heated with zinc and sulphuric acid, or with tin and hydrochloric acid; a rather violent reaction soon sets in, and the nitrobenzene dissolves in the acid, a salt of aniline being produced. Aniline is also formed by heating nitrobenzene with soda-solution, and arsenic trioxide or grape-sugar, or by the action of an alcoholic solution of ammonium sulphide upon nitrobenzene:—

$$C_6H_5.NO_2 + 3H_2S = C_6H_5.NH_2 + 2H_2O + S_3$$

Aniline occurs also in the heavy oils from coal-tar; and it was first obtained by distilling indigo with caustic potash. (*Anil* is the Portuguese name for indigo.)

Aniline is now manufactured on the large scale from commercial benzene, which is first converted into nitrobenzene by acting on it with a mixture of sulphuric and nitric acids. The nitrobenzene is mixed with acetic acid, and iron borings or turnings are gradually added to the liquid until a semi-solid mass is formed, which, after adding some lime, is submitted to distillation in iron retorts.

Commercial aniline always contains amido-toluenes and other bases.

Aniline is a colourless, refractive liquid, boiling at 181°, and solidifying at – 8° to a crystalline mass; when exposed to the air and light, it assumes a brown colour. It has a peculiar, not unpleasant smell, and is very sparingly soluble in water, but freely in alcohol, ether and benzene.

With acids it forms salts, most of which crystallize well.

Aniline hydrochloride $C_6H_5.NH_2.ClH$ crystallizes in needles, which can be sublimed; with platinum chloride it forms the double salt $2(C_6H_5.NH_2.ClH) + PtCl_4$, which crystallizes from water in yellow needles. The hydrochloride forms also crystallized double-salts with zinc chloride, stannic chloride, and other metallic chlorides.

The *nitrate* $C_6H_5.NH_2.NO_3H$ crystallizes in large rhombic plates. The *sulphate* $2(C_6H_3.NH_2)SO_4H_2$ is a white crystalline powder, tolerably soluble in water, less in alcohol, and insoluble in ether.

With oxidizing agents aniline yields very characteristic reactions. Thus, when a solution of bleaching-powder is added to an aqueous solution of aniline, a deep purple colour is produced, which after some time changes into a dirty red. By bringing aniline in contact with sulphuric acid and potassium dichromate, the liquid assumes a pure blue colour, which soon disappears again. A similar colour is produced by the action of hydrochloric acid and potassium chlorate; it also soon disappears, and a dark-green precipitate is formed.

Aniline combines readily with the iodides and bromides of the alcohol radicals, and comports itself in this reaction like an amine, and for this reason it was formerly called *phenylamine*.

Methylaniline $C_6H_5N\left\{\begin{matrix}H\\CH_3\end{matrix}\right.$.—When aniline is mixed with methyl-iodide, a violent reaction sets in, and on cooling the liquid solidifies to a crystalline mass of *methylaniline hydriodide*. The free base is a colourless liquid, resembling aniline, and boiling at 192°. It is also produced, together with dimethylamine, by heating aniline hydrochloride with methyl alcohol under a very great pressure:—

$$C_6H_5.NH_2.ClH + CH_3.OH = C_6H_5.N\left\{\begin{matrix}H\\CH_3\end{matrix}\right\}ClH + H_2O$$

$$C_6H_5N\left\{\begin{matrix}H\\CH_3\end{matrix}\right\}ClH + CH_3.OH = C_6H_5N(CH_3)_2ClH + H_2O$$

Ethylaniline $C_6H_5N\left\{\begin{matrix}H\\C_2H_5\end{matrix}\right.$ boils at 204°, and *diethylaniline* $C_6H_5\left\{\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right.$ at 213°. The latter compound combines with ethyl-iodide; and the iodide of the compound ammonium thus formed yields, on treatment with moist silver oxide, the strongly alkaline and caustic *triethylphenylammonium hydroxide* $N(C_6H_5(C_2H_5)_3)OH$, which, by the action of heat, is resolved into diethylaniline, ethylene, and water.

Phenylaniline or *diphenylamine* $\left.\begin{matrix}C_6H_5\\C_6H_5\\H\end{matrix}\right\}N$ is formed when a mixture of aniline and aniline hydrochloride is heated under pressure. It is a crystalline solid, melting at 45°, boiling at 310°, and possessing a peculiar smell, like flowers. With acids it forms salts, which are decomposed by water. With nitric acid it yields an intensely blue liquid.

Methyl-phenyl-aniline 6 $\left.\begin{array}{c} C_2H_5 \\ C_6H_5 \\ CH_2 \end{array}\right\}N$ is formed by acting with methyl-aniline on aniline hydrochloride at 280° for thirty-six hours. It is a liquid, boiling at 270°, and yielding, when heated with hexachlorethene, a magnificent blue-violet colouring matter.

Diphenylaniline or triphenylamine $\left.\begin{array}{c} C_6H_5 \\ C_6H_5 \\ C_6H_5 \end{array}\right\}N$.—Potassium dissolves readily in aniline, forming the compounds $C_6H_5.NHK$ and $C_6H_5.NK_2$, which, when heated with bromobenzene, are converted into phenylaniline and diphenylaniline. It is a solid, crystallizing from petroleum-spirit in thick, large plates, melting at 126°, and boiling at a very high temperature. It has no basic properties, and gives, with oxidizing agents, blue or green colorations.

ANILIDES.

Just as the ammonium-salts of many acids are resolved by heat into water and an amide, the salts of aniline yield by the same reaction anilides.

Formanilide $C_6H_5.N\left\{\begin{array}{l} COH \\ H \end{array}\right.$ is produced by heating aniline with ethyl formate, as well as when aniline oxalate is quickly heated. It forms colourless crystals, melting at 46°. It is freely soluble in hot water, and yields, by distillation with hydrochloric acid, benzonitrile $C_6H_5.CN$.

Acetanilide $C_6H_5N\left\{\begin{array}{l} CO.CH_3 \\ H \end{array}\right.$.—This body may be obtained by the action of acetyl chloride or acetic anhydride upon aniline, or by the distillation of aniline acetate. It is sparingly soluble in cold water, and crystallizes from a boiling solution in shining plates, melting at 106°, and boiling at 292°. It dissolves in fuming nitric acid with the formation of nitro-acetanilide, and, by the action of chlorine or bromine, it yields substituted acetanilides.

Carbanilamide or *phenyl-urea* $CO\left\{\begin{array}{l} NH.C_6H_5 \\ NH_2 \end{array}\right.$ has been produced by passing the vapour of cyanic acid into well-cooled aniline, and by evaporating a solution of aniline sulphate with potassium cyanate. It is almost insoluble in hot water, and crystallizes from a boiling solution in white needles.

Carbanilide or *diphenyl-urea* is formed together with ammonia and cyanuric acid when phenyl-urea is heated, and it is also obtained by the action of carbonyl chloride on aniline, and by heating aniline with urea;—

$$2C_6H_5.NH_2 + CO\left\{\begin{matrix}NH_2\\NH_2\end{matrix}\right. = CO\left\{\begin{matrix}NH.C_6H_5\\NH.C_6H_5\end{matrix}\right. + 2NH_3$$

It crystallizes in silky white needles; is insoluble in water and volatilizes on heating.

Ethyl carbanilate or *phenyl-urethane* $CO\left\{\begin{matrix}NH(C_6H_5)\\OC_2H_5\end{matrix}\right.$ is found when aniline is acted upon by chlorocarbonic ether (page 118). It forms large crystals, and boils at 237°. By heating it with phosphorus pentoxide, it is resolved into ethyl alcohol and *carbanil* or *phenyl carbimide* $\left.\begin{matrix}C_6H_5\\CO\end{matrix}\right\}N$, a very refractive liquid, boiling at 163°, and possessing a most pungent smell.

When this body is brought in contact with a little triethylphosphine, it is converted into the polymeric *diphenyl dicarbimide* (phenyl dicyanate) $\left.\begin{matrix}(C_6H_5)_2\\(CO)_2\end{matrix}\right\}N_2$, forming large beautiful crystals, melting at 175°. At a high temperature it is resolved again into two molecules of carbanil. It combines with alcohol, forming *ethyl diphenylallophanate* $C_6H_5.N\left\{\begin{matrix}CO.NH(C_6H_5\\CO.OC_2H_5\end{matrix}\right\}$ (see page 120), crystallizing in fine needles, melting at 98°.

Sulphocarbanilide $CS\left\{\begin{matrix}NH.C_6H_5\\NH.C_6H_5\end{matrix}\right.$ is produced by boiling an alcoholic solution of aniline and carbon disulphide as long as hydrogen sulphide is given off. It forms iridescent plates, which are sparingly soluble in water, more freely in alcohol, and have a bitter taste.

Phenylsulphocarbimide or Phenyl mustard-oil $\left.\begin{matrix}C_6H_5\\CS\end{matrix}\right\}N$.—To prepare this compound, sulphocarbanilide is heated with fuming hydrochloric acid. It is a colourless liquid, boiling at 222°, and smelling like common mustard-oil.

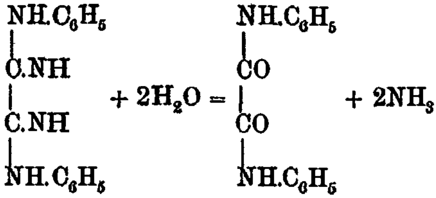
Oxanilide $(C_6H_5)_2N_2H_2.C_2O_2$ is obtained, together with formanilide, when aniline oxalate is heated. It is insoluble in water, and sublimes on heating in shining crystals, melting at 245°. By heating aniline with an excess of oxalic acid, the monobasic *oxanilic acid* $C_6H_5N\left\{\begin{matrix}H\\C_2O_2.OH\end{matrix}\right.$ is formed, which is soluble in water.

Cyananilide $C_6H_5N\left\{\begin{matrix}N\\CN\end{matrix}\right.$ is formed by passing cyanogen chloride into a solution of aniline in ether. It is an amorphous mass.

Melaniline or *diphenyl-guanidine* $C(NH)(NH.C_6H_5)_2$ is a weak base, forming crystalline salts, and is produced by passing cyanogen chloride into pure aniline. An isomeric compound is formed when guanidine hydrochloride is gently heated with aniline. The isomerism of these two compounds is most probably caused by two phenyl groups replacing different atoms of hydrogen in guanidine $C(NH)(NH_2)_2$.

Carbotriphenyl-triamine or *triphenyl-guanidine* $C(NH)\left\{\begin{array}{l}NH.C_6H_5\\ N(C_6H_5)_2\end{array}\right.$ is a mon-acid base, which is formed by the action of tetrachloromethane CCl_4 on aniline. It is a crystalline solid, insoluble in water, and forming crystallized salts.

Cyaniline $C_2(NH)_2(NH.C_6H_5)$.—On passing cyanogen gas into an alcoholic solution of aniline, this compound separates out after some time. It is a crystalline solid, combining with acids. On heating it with aqueous acids, it is decomposed with formation of ammonia, and oxanilide or oxamide:—



$$\begin{array}{l}NH.C_6H_5\\ |\\ C.NH\\ |\\ C.NH\\ |\\ NH.C_6H_5\end{array} + 2H_2O = \begin{array}{l}NH.C_6H_5\\ |\\ CO\\ |\\ CO\\ |\\ NH.C_6H_5\end{array} + 2NH_3$$

Cyanobenzene or Phenyl Carbamine $CN.C_6H_5$.—This compound is obtained by the distillation of a mixture of aniline, chloroform, and caustic potash. It is liquid, boiling, with partial decomposition, at 160°. Its colour appears blue in reflected light, and green by transmitted light. It has a most penetrating odour, like other carbamines. By acids it is decomposed with the formation of aniline and formic acid.

SUBSTITUTED ANILINES.

Monochloraniline $C_6H_4Cl.NH_2$ is prepared by acting with strong nitric acid on chlorobenzene, and treating the nitrochlorobenzene thus formed with a reducing agent. Monochloraniline is insoluble in cold water, very sparingly soluble in boiling water, but readily in alcohol. It crystallizes in shining octahedrons, and is a weak base, forming crystalline salts.

Dichloraniline $C_6H_3Cl_2.NH_2$ and *trichloraniline* $C_6H_2Cl_3.NH_2$ are crystalline solids, having no basic properties. Trichloraniline is also formed, together with small quantities of the two other chloranilines, by the action of chlorine upon aniline, the greatest part of which, however, is converted into a dark tarry mass.

Monobromaniline $C_6H_4Br.NH_2$ has been obtained from monobrombenzene, and has great resemblance with chloraniline.

Dibrom- and tribromaniline are produced by the action of bromine upon aniline, as well as by heating nitrobenzene with hydrobromic acid:—

$$C_6H_5.NO_2 + 6HBr = C_6H_5.NH_2 + 3Br_2 + 2H_2O$$

The nitrobenzene being first reduced to aniline, free bromine is formed, which substitutes hydrogen in aniline.

Iodaniline $C_6H_4I.NH_2$ is readily formed by the action of iodine upon aniline, but it is not produced by heating nitrobenzene with hydriodic acid, because free iodine acts only upon free aniline, but not on its salts. Iodaniline is a weak base, crystallizing in white prisms.

Orthonitraniline $C_6H_4\left\{\begin{matrix}NH_2\\NO_2\end{matrix}\right.$.—This compound is not formed by the action of nitric acid upon aniline. To obtain it, an anilide, as acetanilide, is dissolved in strong nitric acid, and the nitro-acetanilide thus formed boiled with potash-solution :—

$$C_6H_4\left\{\begin{matrix}NH.C_2H_3O\\NO_2\end{matrix}\right. + KOH = C_6H_4\left\{\begin{matrix}NH_2\\NO_2\end{matrix}\right. + C_2H_3O_2K$$

Orthonitraniline crystallizes in long yellow needles or plates, melting at 146° and subliming without decomposition.

Paranitraniline $C_6H_4\left\{\begin{matrix}NH_2\\NO_2\end{matrix}\right.$.—This isomeride is obtained by reducing dinitrobenzene with an alcoholic solution of ammonium sulphide. It forms yellow needles, melting at 110°, and subliming readily on heating.

Paranitraniline is the starting-point for a series of substituted anilines, which are isomeric with those just described. To obtain these paranitraniline is converted, first, into a diazo-compound, and this decomposed by hydrochloric, hydrobromic, or hydroiodic acid. The substituted nitrobenzenes thus formed are then reduced by a suitable agent.

Parachlor- and *parabromaniline* are liquids. *Para-iodaniline* crystallizes in silvery scales, melting at 25°.

Metanitraniline.—By the action of nitric acid on bromobenzene, two isomeric bromonitrobenzenes are formed, one melting at 125°, and the other at 38°. When the former is treated with concentrated alcoholic ammonia for twelve hours to 190°, it is converted into orthonitraniline, whilst the second modification yields by this reaction metanitraniline; which is more volatile and more soluble than its two isomerides. It forms yellow needles, melting at 66°; its aqueous solution stains the skin yellow.

The nitranilines are weak bases, forming salts, which are decomposed by water.

Sulphanilic Acid or Amidobenzene-sulphonic Acid $C_6H_4\left\{\begin{matrix}NH_2\\SO_2.OH\end{matrix}\right.$.—This powerful monobasic acid is obtained by dissolving aniline in fuming sulphuric acid. It is not freely soluble in cold water, and crystallizes from a hot solution in rhombic plates containing one molecule of water. Its salts are soluble in water, and crystallize well.

Thio-aniline $S\left\{\begin{matrix}C_6H_4.NH_2\\C_6H_4.NH_2\end{matrix}\right.$.—This bi-acid base is formed together with hydrogen sulphide by heating aniline and sulphur together with oxide of lead, the latter being added to remove the hydrogen sulphide as soon as it is formed, because it has a decomposing action on thio-aniline.

Thio-aniline crystallizes from a hot aqueous solution in long, thin silky needles, melting at 104°; when more strongly heated, they are decomposed. With acids it combines, forming salts which all crystallize very readily. On adding potassium dichromate to the solution of one of the salts, violet flakes, soluble in alcohol, are precipitated. Thio-aniline dissolves in concentrated sulphuric acid, forming a red or blue solution, which, when poured into water, yields a beautiful red liquid.

DIAMIDOBENZENES $C_6H_4\left\{\begin{matrix}NH_2\\NH_2\end{matrix}\right.$.

Orthodiamidobenzene is formed by the reduction of orthonitraniline; it is readily soluble in water, and forms colourless crystals, melting at 140°, and boiling at 267°.

Paradiamidobenzene has been prepared by reducing dinitrobenzene or paranitraniline with tin and hydrochloric acid. On decomposing the hydrochloride thus formed with soda, the base separates out as a liquid, which gradually solidifies to a crystalline mass. It melts at 63°, and boils at 287°. It absorbs oxygen from the air, and changes soon into a brown mass.

Metadiamidobenzene is obtained from metanitraniline. It forms brilliant white plates, melting at 99° and boiling at 252°.

TRIAMIDOBENZENE $C_6H_3\left\{\begin{matrix}NH_2\\NH_2\\NH_2\end{matrix}\right.$.

When triamidobenzoic acid is heated, it is resolved into carbon-dioxide and triamidobenzene, a crystalline solid, melting at 104°, and boiling at 330°. Its concentrated aqueous solution has an alkaline reaction, and gives, with ferric chloride, a violet precipitate, which soon turns brown. It reduces an ammoniacal silver solution, and gives, with sulphuric acid containing a trace of nitric acid, a deep blue liquid. Triamidobenzene forms crystalline salts, containing two equivalents of an acid.

AZO-DERIVATIVES OF BENZENE.

Azobenzene $\left.\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\right\}N_2$ is obtained by distilling nitrobenzene with an alcoholic solution of potash. In this reaction the alcohol acts as a reducing agent, being oxidized to aldehyde. Azobenzene is also produced by the action of sodium amalgam on an alcoholic solution of nitrobenzene, and, but in a small quantity only, by oxidizing aniline hydrochloride with potassium permanganate.

It crystallizes in large yellowish-red plates, melting at 66°·5, and boiling at 293°, and possessing a faint smell of roses. Concentrated nitric acid converts it into nitro-compounds, and sulphuric acid dissolves it in the cold without acting on it; but on heating the solution *azobenzenesulphonic acid* $C_{12}H_9N_2SO_3H$ is formed, which, as well as its salts, readily crystallizes.

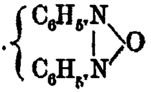
Azobenzene readily combines with bromine, forming *azobenzene dibromide* $C_6H_{10}N_2Br_2$, crystallizing in golden-yellow needles. Reducing agents, as ammonium sulphide, convert it into *hydrazobenzene* $C_{21}H_{10}N_2H_2$, a compound which is also obtained, together with azobenzene, by the oxidation of aniline hydrochloride. It crystallizes in colourless plates, smelling like camphor. Oxidizing agents convert it into azobenzene, and by distillation it is resolved into aniline and azobenzene.

Dinitrohydrazobenzene $C_{12}H_8(NO_2)_2N_2H_2$ is formed by the action of cold ammonium sulphide on dinitro-azobenzene. It crystallizes from boiling alcohol in large yellow needles, melting at 220°; by heating above this temperature, it is resolved into dinitro-azobenzene and paranitraniline.

Diamidohydrazobenzene or *Diphenine* $C_{12}H_8(NH_2)_2N_2H_2$ is a yellow crystalline base, obtained by boiling dinitro-azobenzene with alcoholic ammonium sulphide. By the further action of reducing agents, it is resolved into two molecules of diamidobenzene.

Azoxybenzene $C_{12}H_{10}N_2O$ is formed together with azobenzene by reducing nitrobenzene with alcoholic potash. It crystallizes in long yellow needles.

These azo-compounds are bodies standing intermediate between nitrobenzene and amidobenzene; their constitution is explained by the following formulæ:—

Nitrobenzene	$C_6H_5.NO_2$
Azoxybenzene	 $\left\{\begin{array}{l} C_6H_5.N \\ \quad\ \ \vert \ \rangle O \\ C_6H_5.N \end{array}\right.$
Azobenzene	$\left\{\begin{array}{l} C_6H_5.N \\ \qquad\ \ \Vert \\ C_6H_5.N \end{array}\right.$
Hydrazobenzene . . .	$\left\{\begin{array}{l} C_6H_5.NH \\ \qquad\ \ \vert \\ C_6H_5.NH \end{array}\right.$
Amidobenzene	$C_6H_5.NH_2$

DIAZOBENZENE COMPOUNDS.

These compounds are produced by acting with nitrous acid on a salt of aniline; thus aniline nitrate yields *diazobenzene nitrate*:—

$$C_6H_5.NH_2NO_3H + HNO_2 = C_6H_5N_2.NO_3 + 2H_2O$$

The monad radical diazobenzene has the constitution $C_6H_5.N{=}N-$; its compounds are very unstable bodies, and easily decomposed by water, absolute alcohol, and acids. Thus, on boiling a diazobenzene compound with absolute alcohol, it is reduced to benzene:—

$$C_6H_5N_2.NO_3 + C_2H_6O = C_6H_6 + C_2H_4O + NO_3H + N_2$$

When it is boiled with water, it yields phenol—

$$C_6H_5N_2.NO_3 + H_2O = C_6H_5.OH + NO_3H + NO_3H$$

whilst concentrated hydriodic acid converts it into moniodobenzene:—

$$C_6H_5N_2.NO_3 + HI = C_6H_5I + NO_3H + N_2$$

The substituted anilines are acted on by nitrous acid in precisely the same manner, and the diazobenzene compounds are, therefore, of great theoretical interest; as by means of them not only a large number of substitution-products may be obtained by simple reactions, but also the positions of the side-chains in isomeric bodies can be fixed, if we either start with such of known constitution, or if we obtain compounds in which the positions of the side-chains have been ascertained by other reactions.

Thus paranitraniline yields diazobenzene compounds, which, by the action of hydrochloric, hydrobromic, or hydriodic acids, are converted into the corresponding substituted nitrobenzenes, in which, as well as in paranitraniline and paradiamidobenzene, the side-chains occupy the positions 1, 4, inasmuch as the paranitro-iodobenzene thus formed yields by reduction para-iodaniline, and this compound, by converting it again into a diazo-compound, and boiling the latter with water, is transformed into para-iodophenol (see page 314).

In metanitraniline and metadiamidobenzene, the side-chains have the positions 1, 2. This follows from the following considerations:— Para-oxybenzoic acid belongs to the group 1, 4 (see page 314; to the same group belongs, therefore, para-amidobenzoic acid $C_6H_4\begin{cases}CO_2H\\NH_2\end{cases}$, inasmuch as it yields a diazo-compound, which by boiling water is converted into para-oxybenzoic acid. The amido-acid can yield two nitro-compounds: in one of these the nitroxyl has the position $2 = 6$ and in the other $3 = 5$. One of these yields, by acting on it with an alcoholic solution of nitrous acid, common nitrobenzoic acid belonging to the group 1, 3; consequently in the corresponding nitro-amidobenzoic acid the groups NH_2 and NO_2 are linked to two adjoining carbon-atoms, or in the positions 3, 4 = 1, 2. Now, as by reduction this nitro-acid yields a diamidobenzoic acid, which, by the action of heat, is resolved into carbon dioxide and metadiamidobenzene, it follows that the latter compound belongs to the group 1, 2.

As we know now the constitution of two diamidobenzenes, we know also that of orthodiamidobenzene, which, as well as its derivatives, belong to the group 1, 3.

The different substituted anilines obtained by the above reactions can again be transformed into diazo-compounds, and the latter into isomeric dichloro-, dibromo-, or di-iodobenzenes. Now, as from all these bodies new nitro- and amido-compounds may be produced, and the latter again converted into diazo-compounds, it is readily understood how important the diazo-compounds are from a theoretical point of view.

Diazobenzene Nitrate $C_6H_5N_2.NO_3$.—To prepare this compound, water is added to an excess of aniline nitrate, and nitrogen trioxide passed into the liquid. The solution becomes warm, and soon the salt appears in crystals, the yield of which is increased by adding a mixture of alcohol and ether. It forms colourless needles, sparingly soluble in alcohol, and insoluble in ether. The dry salt detonates by heat or percussion with the greatest violence.

Diazobenzene Sulphate $C_6H_5N_2.SO_4H$ is obtained by decomposing a concentrated solution of the nitrate with dilute sulphuric acid, and adding alcohol and ether to the liquid. It crystallizes in colourless prisms, and is very explosive. When to its solution a solution of platinic chloride in hydrochloric acid is added, the compound $(C_6H_5N_2Cl)_2 + PtCl_4$ separates in fine yellow prisms.

Diazobenzene-potassoxide $C_6H_5N_2.OK$.—This compound is obtained by adding potash-solution to a salt of diazobenzene. It separates as a yellow, oily liquid, which, by drying on a water-bath, solidifies to a crystalline mass. The pure compound forms small shining scales, and is readily soluble in water.

Diazobenzene-argentoxide $C_6H_5N_2.OAg$ is a greyish-white and very explosive powder, which is obtained by adding silver nitrate to a solution of the potash-compound.

Diazobenzene Hydroxide $C_6H_5N_2.OH$.—When acetic acid is added to the potash-compound, a yellow oil, possessing an aromatic smell, separates out, which appears to be diazobenzene hydroxide. It is a most unstable body, which in a few moments decomposes with evolution of nitrogen and phenol.

Diazo-amidobenzene $C_6H_5N_2.NH(C_6H_5)$ is produced by adding aniline to an alcoholic solution of diazobenzene salt, and is also obtained by passing nitrogen trioxide into a cold alcoholic aniline solution, or by adding a slightly alkaline solution of potassium nitrite to a solution of aniline hydrochloride. It is insoluble in water, and crystallizes from an alcoholic solution in golden-yellow scales. On heating, it explodes. It does not combine with acids, but yields with platinic chloride and hydrochloric acid a crystallized double salt $(C_{12}H_{11}N_3, ClH)_2 + PtCl_4$.

Amido-azobenzene $C_6H_5.N_2.C_6H_4.NH_2$.—This compound is isomeric with diazo-amidobenzene, and is obtained by leaving the latter in contact with alcohol and an aniline salt. It is also produced by passing nitrogen trioxide into a warm solution of aniline, and by reducing mononitro-azobenzene with ammonium sulphide. Amido-azobenzene crystallizes from alcohol in yellow needles, which sublime at a high temperature; it is found in commerce under the name of *Aniline-yellow.* It is a weak base, forming salts having a red or violet colour, and which are decomposed by water.

On heating it with tin and hydrochloric acid, it takes up hydrogen, and is resolved into aniline and diamidobenzene :—

$$C_{12}H_{11}N_3 + 2H_2 = C_6H_7N + C_6H_8N_2$$

This reaction shows that it has the following constitution :—

$$C_6H_5—N{=}N—C_6H_5.NH_2$$

whilst the isomeric diazo-amidobenzene is :—

$$C_6H_5—N{=}N—NH.C_6H_5$$

We do not yet know why diazo-amidobenzene, when in contact with an aniline salt, undergoes such a molecular change; a small quantity of the latter being sufficient to transform a large quantity of diazo-amidobenzene into amido-azobenzene.

Triamido-azobenzene $N_2\left\{\begin{matrix}C_6H_4.NH_2\\C_6H_3.(NH_2)_2\end{matrix}\right.$.—The hydrochloride of this base forms the principal portion of *Phenylene-brown,* a colouring matter used for dyeing woollen goods, which is manufactured by adding a solution of sodium nitrite to a cold, dilute solution of *paramidobenzene hydrochloride.* The mode of formation of this base is quite analogous to that of aniline-yellow. The *diazo-diamidobenzene,* which is first formed, undergoes a molecular change, and is transformed into triamido-azobenzene.

Diazo-diamidobenzene $H_2N.C_6H_4.N_2.NH.C_6H_4.NH_2$

Triamido-azobenzene $H_2N.C_6H_4.N_2.C_6H_3\left\{\begin{matrix}NH_2\\NH_2\end{matrix}\right.$

OXYBENZENES, OR PHENOLS.

Monoxybenzene, or Common Phenol $C_6H_5.OH$.—This compound, which is also known by the names "carbolic acid" or "phenyl alcohol," is produced in quantity by the destructive distillation of coal, wood, and other organic substances. It occurs in small quantity in human urine, and in the urine of herbivorous animals, and in castoreum.

Phenol has been obtained synthetically by dissolving acetylene in fuming sulphuric acid, and fusing the sulpho-acid thus formed with caustic potash:—

$$3C_2H.SO_3K + 3KOH = C_6H_5.OH + 2K_2SO_4 + K_2SO_3$$

Phenol is manufactured on the large scale by agitating heavy coal-tar oil, boiling above 150°, with a concentrated soda-solution, to which some solid caustic soda is added. A crystalline magma is formed, whilst neutral oils are left undissolved. After the latter have been separated, the soda-compound is decomposed with hydrochloric acid, and the impure phenol again treated with a quantity of soda, which is insufficient to dissolve the whole; phenol dissolving in alkalis more readily than cresol and other homologues, which are present in the crude product. The solution is exposed to the air, in order to remove impurities which are easily oxidized, and soon separate as a tarry matter. The clear liquid is then treated with hydrochloric acid, and the phenol, after being dried over calcium chloride, is submitted to fractional distillation. From the portion boiling below 190°, phenol separates out in crystals on cooling.

Pure phenol may also be obtained by heating salicylic acid (oxy-benzoic acid) with quicklime; this reaction is quite analogous to the formation of benzene from benzoic acid:—

$$C_6H_4\left\{\begin{matrix}OH\\CO.OH\end{matrix}\right. = C_6H_5.OH + CO_2$$

Pure phenol crystallizes in long, colourless needles, melting at 42°, and boiling at 184°. It possesses a characteristic odour and a pungent and caustic taste, producing white blisters on the tongue. It combines with water, forming a crystallized hydrate $2(C_6H_5.OH)+H_2O$, which by distillation is again resolved into water and phenol.

Pure phenol remains unaltered in the air, but the commercial product soon absorbs water, and is converted into a red liquid. It is much used as a disinfectant, and for the conservation of wood, because it possesses the property of preventing putrefaction.

Ferric chloride produces in an aqueous solution of phenol a violet colour; and, with a little ammonia and a solution of bleaching-powder, it yields a fine blue colour. The best reagent for phenol is, however, bromine-water (see tribromophenol).

Methyl-phenyl Ether, or Anisol $\left.\begin{matrix}C_6H_5\\CH_3\end{matrix}\right\}O$.—This compound was first obtained by distilling anisic acid with baryta, and is easily prepared by heating potassium phenate with methyl iodide. It is a coloruless liquid, possessing an aromatic odour, and boiling at 152°. By heating it with hydriodic acid to 130°, it is resolved into methyl iodide and phenol.

Ethyl-phenyl Ether, or *Phenetol* $C_6H_5.O.C_2H_5$, is obtained in a similar way from ethyl iodide; it is an aromatic liquid, boiling at 172°.

Ethene-diphenyl Ether $\left.\begin{matrix}C_6H_5O\\C_6H_5O\end{matrix}\right\}C_2H_4$ is obtained by heating ethene bromide with potassium phenate. It is insoluble in water, and crystallizes from ether in shining scales, melting at 98°·5.

Diphenyl Ether $\left.\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\right\}O$ is formed by the action of phenol upon diazobenzene sulphate:—

$$C_6H_5N_2.SO_4H + C_6H_5.OH = \left.\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\right\}O + SO_4H_2 + N_2$$

It is a crystalline solid, possessing an agreeable odour, melting at 28°, and boiling at 246°. This ether is a most stable compound, which is not reduced by red-hot zinc-dust, and not acted upon by chromic acid, nor altered by heating it with concentrated hydriodic acid.

Phenylphosphoric Acid $\left.\begin{matrix}C_6H_5\\H_2\end{matrix}\right\}PO_4$ is formed together with diphenylphosphoric acid, by the action of phenol on phosphorus pentoxide.

Triphenyl phosphate $(C_6H_5)_3PO_4$ is a colourless, crystalline substance, which is formed, together with chlorobenzene, by the distillation of phenol with phosphorus pentachloride.

Phenyl Carbonate $CO\left\{\begin{matrix}OC_6H_5\\OC_6H_5\end{matrix}\right.$ is produced by heating phenol and carbonyl chloride in closed tubes to 140° to 150°. It crystallizes from alcohol in brilliant silky needles, melting at 78°. On heating, it gives off an agreeable aromatic odour, and sublimes in long needles. With potash solution, it yields potassium carbonate and potassium phenate.

Phenyl Acetate or *Acetyl-phenol Ether* $\left.\begin{matrix}C_6H_5\\C_2H_3O\end{matrix}\right\}O$ is formed by the action of acetyl chloride on phenol, and has also been obtained by heating anhydrous lead acetate with carbon disulphide and phenol:—

$$4C_6H_5.OH + 2\left(\left.\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\right\}O_2Pb\right) + CS_2 =$$

$$4\left(\left.\begin{matrix}C_6H_5\\C_2H_3O\end{matrix}\right\}O\right) + 2PbS + CO_2 + 2H_2O$$

It is a colourless liquid, possessing a peculiar smell, and the same index of refraction as soft German glass; if, therefore, such a glass tube be dipped into the liquid, it becomes invisible. It boils at 200°.

Phenyl Sulphydrate, or Thiophenol $C_6H_5.SH$.—This body has been produced by reducing benzenesulphonic chloride with zinc and dilute sulphuric acid; and it may also be prepared by the action of phosphorus pentasulphide on phenol. It is a colourless, strongly refractive liquid, boiling at 165°, and possessing a penetrating, disagreeable smell Like other mercaptans, it forms readily metallic compounds.

Phenyl Sulphide $\left.\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\right\}S$ is formed, together with thiophenol, by the action of phosphorus pentasulphide on phenol, and is also produced by the dry distillation of sodium benzenesulphonate. It is a limpid liquid, boiling at 292°, and possessing a disagreeable alliaceous smell. Nitric acid oxidizes it to sulphobenzide.

Phenyl Disulphide $\left.\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\right\}S_2$ is obtained, as the first product, when thiophenol is heated with dilute nitric acid, and forms shining white needles. By the action of nascent hydrogen, it is again converted into thiophenol; and by boiling it for a long time with nitric acid, it is oxidized to benzenesulphonic acid.

Phenolsulphonic Acid $C_6H_4\left\{\begin{matrix}OH\\SO_3H\end{matrix}\right.$.—Two isomeric acids having this composition are known, both being formed by the action of concentrated sulphuric acid on phenol. When a solution of phenol on sulphuric acid is left for a few days, the chief product consists of *metaphenolsulphonic acid*, and only a small quantity of *paraphenolsulphonic acid* is formed; whilst, on heating the mixture gently, more of the latter is obtained, and by exposing it to a temperature of 100°—110°, the meta-acid is completely converted into the para-acid.

To obtain the free acids, the insoluble basic lead-salts are decomposed by hydrogen sulphide, and the solution first concentrated on a water-bath, and then evaporated *in vacuo;* they form needle-shaped crystals. The meta-acid is not easily obtained perfectly pure, as on heating its solution a part is always converted into the para-acid. Both form crystalline salts; those of the para-acid are less soluble in water than the meta-salts, and crystallize in different forms.

The side-chains in the meta-acid have the position 1, 3, as on fusion with potash it yields pyrocatechin, whilst the para-acid belongs to the series 1, 4; as by fusing it with potash it is converted into resorcin (see page 314).

Phenoldisulphonic Acid $C_6H_3\left\{\begin{matrix}SO_3H\\OH\\SO_3H\end{matrix}\right.$ is obtained by heating phenol with a large quantity of concentrated sulphuric acid for a long time. On neutralizing the dilute solution with barium carbonate, and evaporating the filtrate, the barium salt $C_6H_3.OH(SO_3)_2Ba + 4H_2O$ is obtained in large prismatic crystals. The free acid is very soluble in water, and crystallizes in small needles. Phenoldisulphonic acid may also be produced by decomposing diazobenzene sulphate with concentrated sulphuric acid. Ferric chloride colours the free acid, as well as its salts, ruby-red.

NITROPHENOLS.

Mononitrophenol $C_6H_4(NO_2)OH$ exists in three isomeric modifications, of which, however, two only have been carefully examined. They are formed together by the action of cold nitric acid (of 20 per cent.) on pure phenol, and separated by submitting the mixture to a current of steam, by which only one modification is volatilized. The *volatile mononitrophenol* is but sparingly soluble in water, more freely in alcohol, and crystallizes in long, transparent, yellow needles, melting at 45°, and boiling at 214°. It has a sweet taste, and an aromatic odour.

The second compound has been called *orthonitrophenol*; it crystallizes from boiling water in brilliant, colourless needles, assuming a red colour in the light. It melts at 110°, and volatilizes at a high temperature.

The solutions of both compounds have an acid reaction, and they decompose carbonates; their salts crystallize well; the silver salts are insoluble in water; that of the volatile nitrophenol has a deep orange colour, and silver orthonitrophenate is a scarlet precipitate.

a Dinitrophenol $C_6H_3(NO_2)_2OH$ is obtained by acting with nitric acid of specific gravity 1·37 on orthonitrophenol. It crystallizes from boiling water in yellowish-white striated plates, melting at 114°, and is a strong monobasic acid.

β Dinitrophenol is formed together with the *a* compound and trinitrophenol by the action of nitric acid on the volatile nitrophenol. The two dinitrophenols are separated by preparing the barium salts, which are repeatedly re-crystallized; barium *a* dinitrophenate being much more soluble than the salt of the *β* compound. *β* dinitrophenol crystallizes from water in short, pointed, yellow needles, and from benzene in long, thick needles, melting at 64°.

Trinitrophenol or *Picric Acid* $C_6H_2(NO_2)_3OH$ is the final product of the action of nitric acid on phenol, as well as on many other bodies containing the aromatic nucleus, such as salicin, indigo, gum-benzoin, balsam of Peru, acaroid-resin, aloes, silk, wool, &c. It is obtained on the large scale by heating phenol with nitric acid until the action ceases.

Pure picric acid crystallizes from water and alcohol in pale-yellow plates, and from ether in fine prisms, melting at 122°·5. When carefully heated it sublimes, but on heating it quickly it decomposes with deflagration. It has an intensely bitter taste, and is but slightly soluble in cold water, and more freely in boiling water.

By acting on it with a solution of bleaching-powder, it yields chloropicrin CCl_3NO_2 (see page 102) and tetrachloroquinone CCl_4O_2.

Picric acid is much used for dyeing silk and wool yellow. Its crystalline salts have a yellow or orange colour.

Potassium picrate $C_6H_2(NO_2)_3OK$ is but slightly soluble in cold water, and crystallizes in long, shining yellow needles; by heat and by percussion it explodes with an extraordinary violence, and is therefore used for the preparation of explosives.

The picrates of sodium, ammonium, barium, and silver are readily soluble in water.

Ethyl picrate $C_6H_2(NO_2)_3OC_2H_5$ is produced by the action of ethyl iodide upon dry silver picrate. It crystallizes in long, pale-yellow needles, which on heating first melt, and then decompose with a slight explosion.

By the action of phosphorus pentachloride upon picric acid, *trinitrochlorobenzene* $C_6H_2(NO_2)_3Cl$ is obtained, a crystalline solid, having an aromatic smell. This compound has been also called *picryl chloride*, because it is decomposed by water, analogous to other acid chlorides, into picric acid and hydrochloric acid.

This reaction shows how the character of an aromatic compound is modified when hydrogen is replaced by nitroxyl. Whilst monochlorobenzene is not acted on by caustic potash, its trinitro-compound is readily decomposed by water.

Trinitro-amidobenzene, or *Picramide* $C_6H_2(NO_2)_3NH_2$, is produced by acting with ammonium carbonate on picryl chloride, or by heating ethyl picrate with alcoholic ammonia. It crystallizes from glacial acetic acid in glistening yellow plates, melting at 187°. On heating it stronger, it decomposes without explosion; and, by boiling it with caustic potash, it yields ammonia and potassium picrate.

Picric acid combines with aromatic hydrocarbons, forming compounds which are distinguished by their characteristic colours or crystalline forms. This acid is, therefore, often used for the detection or separation of such hydrocarbons. Thus on dissolving picric acid in hot benzene, the compound $C_6H_6 + C_6H_2(NO_2)_3OH$ separates out on cooling in pale-yellow transparent crystals, melting at 149°; it dissolves, without decomposition, in alcohol and ether; but when exposed to the air, benzene is slowly given off, whilst alkalis decompose it at once.

Isopurpuric Acid, or Picrocyamic Acid $C_8H_5N_5O_6$.—The potassium salt of this acid is formed by dissolving picric acid in a solution of potassium cyanide:—

$$C_6H_3N_3O_7 + 3CNK + 2H_2O = C_8H_4N_5O_6K + CO_3K_2 + NH_3$$

Potassium isopurpurate crystallizes in reddish-brown scales, having a beetle-green lustre, and dissolving in water and alcohol with an intensely red colour; it explodes by heat. The free acid is not known, but a great number of salts have been prepared. The ammonium salt, which is obtained by double decomposition of the potassium salt with sal-ammoniac, has the greatest resemblance to ammonium purpurate or murexide, and is used for dyeing. Barium isopurpurate is a vermilion-red precipitate, which is soluble in hot water.

The isopurpurates are decomposed by acids; the liquid gives off a pungent smell; brown flakes separate out; and on evaporating the brown solution an amorphous residue is left behind.

AMIDO-COMPOUNDS OF PHENOL.

Ortho-amidophenol $C_6H_4\left\{\begin{matrix}OH\\HN_2\end{matrix}\right.$ is obtained by reducing orthonitrophenol with zinc and hydrochloric acid. It is a brown crystalline powder, which on heating sublimes, with partial decomposition, in white needles; it forms, with acids, crystallizable salts. An isomeric compound is produced by the reduction of the volatile nitrophenol; it crystallizes in colourless rhombic plates, which readily sublime; it is also a base,

Diamidophenol $C_6H_3\left\{\begin{matrix}NH_2\\NH_2\end{matrix}\right.$ has not yet been obtained in a pure state.

Dinitro-amidophenol or Picramic Acid $C_6H_2\left\{\begin{matrix}NH_2\\OH\\(NO_2)_2\end{matrix}\right.$.—The ammonium-salt of this compound is formed by the action of hydrogen sulphide on ammonium picrate. By decomposing it with hydrochloric acid, picramic acid is set free; it crystallizes in brilliant red needles, melting at 165°, and forms red-coloured salts.

DIAZOPHENOL-COMPOUNDS.

The chlorides of these compounds are formed by treating the hydrochlorides of the two amidophenols with alcohol which has been saturated with nitrogen trioxide.

Orthodiazophenol chloride $C_6H_4(OH)N_2Cl$ is but slightly soluble in alcohol, and crystallizes in long colourless needles. The second *diazophenol chloride* dissolves more freely in alcohol, and forms colourless rhombohedrons.

Both compounds decompose at 100°, with a slight explosion, and yield, when treated with concentrated hydriodic acid, the corresponding iodophenols. When they are heated with hydrochloric acid, resinous bodies are formed, but no chlorophenols; the latter may, however, be obtained by submitting the platinum double salts to dry distillation.

HALOID SUBSTITUTION-PRODUCTS OF PHENOL.

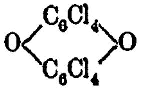
Orthochlorophenol $C_6H_4Cl.OH$ is the first product of the action of chlorine on phenol. It crystallizes in white needles, melting at 41°, and boiling at 218°. It possesses a faint but very disagreeable smell, and is very caustic, producing white blisters on the skin. An isomeric compound has been obtained from the second diazo-compound, as above mentioned. It is a thick oily liquid, having a peculiar aromatic odour, and boiling at about 180°.

Dichlorophenol $C_6H_2\left\{\begin{matrix}Cl_2\\OH\end{matrix}\right.$ is obtained, together with trichlorophenol, by the action of chlorine on phenol or chlorophenol. To separate the two compounds, the mixture is treated with a warm solution of sodium carbonate, by which only the trichlorophenol is dissolved, whilst impure dichlorophenol is left behind as an oily liquid, which is purified by fractional distillation and recrystallization. It crystallizes from benzene in long needles, melting at 43°, and boiling at 209°.

Trichlorophenol $C_6H_2\left\{\begin{matrix}Cl_3\\OH\end{matrix}\right.$ crystallizes in thin white needles, melting at 61°, and boiling at 244°. It possesses a strong, disagreeable odour, and is a monobasic acid.

Tetrachlorophenol $C_6H\left\{\begin{matrix}Cl_4\\OH\end{matrix}\right.$ is not known in a pure state.

Pentachlorophenol or Perchlorophenol $C_6Cl_5.OH$ is readily obtained by the action of chlorine on a mixture of phenol and antimony trichloride. The crude product is purified by distilling it with steam at 180°—200°. It crystallizes from petroleum-naphtha in thin, long, brilliant needles, melting at 187°; its alcoholic solution colours blue litmus red. At the common temperature it is odourless, but when heated it gives off a very pungent odour, and its dust produces violent sneezing. Phosphorus pentachloride converts it into hexachlorobenzene. When its potassium salt is heated, it is resolved into potassium chloride and *perchlorophenylene oxide* C_6Cl_4O, which is insoluble in alcohol and most other solvents, but dissolves freely in boiling nitrobenzene, and crystallizes on cooling in flat needles, resembling benzoic acid. It melts at 320°, and boils above the boiling-point of mercury. As this compound has such a high boiling-point, it has probably the following constitution:—



Monobromophenol $C_6H_4\left\{\begin{matrix}Br\\OH\end{matrix}\right.$ is obtained by dissolving bromine and phenol in glacial acetic acid, and gradually mixing the well-cooled solutions. It forms large colourless crystals, resembling alum; it melts at 64°, and boils at 236°.

Dibromophenol $C_6H_4\left\{\begin{matrix}Br_2\\OH\end{matrix}\right.$ is produced by the further action of bromine, and forms glistening, white crystals, melting at 40°, and subliming even at the common temperature.

Tribromophenol $C_6H_2\left\{\begin{matrix}Br_3\\OH\end{matrix}\right.$ is obtained as a crystalline precipitate by adding bromine water to an aqueous solution of phenol. It is quite insoluble in water, and this reaction may be used for the quantitative determination of phenol, as well as for detecting small quantities of it—for example, in urine, or in drinking water from wells situated near gas-works, &c. Aniline and some other bodies give similar precipitates with bromine water; but that produced by phenol differs from these by being easily reduced to phenol, which can be recognized by its characteristic smell. This reduction is readily effected by treating tribromophenol with dilute sulphuric acid and sodium amalgam.

Tetra- and *Pentabromophenol* are also known; both are crystalline solids.

Moniodophenol $C_6H_4\left\{\begin{matrix}I\\OH\end{matrix}\right.$ exists in three isomeric modifications. The two of these are formed together by acting with iodine and iodic acid on an alkaline solution of phenol:—

$$5C_6H_5.OH + 2I_2 + HIO_3 = 5C_6H_4I.OH + 3H_2O$$

Ortho-iodophenol is also obtained pure by boiling diazo-iodobenzene sulphate with water. It forms flat, glistening needles, possessing a faint but disagreeable smell; nitric acid decomposes it with the separation of iodine.

Meta-iodophenol is an oily liquid, but has not yet been obtained perfectly pure.

Para-iodophenol has been prepared from the diazo-iodobenzene sulphate obtained from para-iodaniline. It crystallizes in needles, and yields, with fuming nitric acid, substitution-products, without iodine being liberated. The same compound is also formed, together with a small quantity of its isomerides, by acting with iodine on phenol in the presence of mercuric oxide:—

$$2C_6H_5.OH + 2I_2 + HgO = 2C_6H_4I.OH + HgI_2 + H_2O$$

DIOXYBENZENES.

The three isomeric dioxybenzenes have been prepared by fusing the iodophenols with caustic potash:—

$$C_6H_4\left\{\begin{matrix}I\\OH\end{matrix}\right. + KOH = C_6H_4\left\{\begin{matrix}OH\\OH\end{matrix}\right. + KI$$

Hydroquinone is prepared by heating ortho-iodophenol with potash to 180°. This body was first obtained by suspending quinone $C_6H_4O_2$ (see below) in water, and passing sulphur dioxide into it until a colourless solution is formed:—

$$C_6H_4\left\{\begin{matrix}O\\O\end{matrix}\right.\!\!> + 2H_2O + SO_2 = C_6H_4\left\{\begin{matrix}OH\\OH\end{matrix}\right. + SO_4H_2$$

Hydroquinone crystallizes in rhombic prisms, melting at 172°, and subliming with partial decomposition at a higher temperature. It exists as glucoside, called *arbutin*, in the leaves of the bearberry (*Arbutus Uva ursi*) and other Ericaceæ; when arbutin is boiled with dilute sulphuric acid, it is resolved into hydroquinone and dextrose;—

$$C_6H_4\left\{\begin{matrix}OH\\OC_6H_{11}O_5\end{matrix}\right. + \left.\begin{matrix}H\\H\end{matrix}\right\}O = C_6H_4\left\{\begin{matrix}OH\\OH\end{matrix}\right. + C_6H_{12}O_6$$

Hydroquinone does not yield substitution-products with bromine and chlorine, because these elements oxidize it first to quinone. But substituted hydroquinones are readily formed by the action of sulphur dioxide and water on chloro- and bromo-quinones.

Dinitrohydroquinone $C_6H_2\left\{\begin{matrix}(OH)_2\\(NO_2)_2\end{matrix}\right.$.—By the action of concentrated nitric acid on arbutin, dinitroarbutin is formed, which, on boiling with very dilute sulphuric acid, is resolved into dextrose, and dinitrohydroquinone. It crystallizes in golden-yellow plates, dissolving with a blue colour in alkalis.

Quinone $C_6H_4\left\{\begin{matrix}O\\O\end{matrix}\right.\!\!>$.—This compound was first obtained by oxidizing quinic acid $C_6H_7(OH)_4CO_2H$ with manganese dioxide and sulphuric acid; and it is also formed by the oxidation of hydroquinone and several other derivatives of benzene.

Quinone is a very volatile body, subliming readily in brilliant golden-yellow needles, possessing a suffocating smell, like iodine. It is but slightly soluble in cold water, more freely in boiling water and alcohol and ether; the solution has a yellow colour, and produces brown stains on the skin.

Quinhydrone, or green Hydroquinone $C_6H_4\left\{\begin{matrix}O.OC_6H_4.OH\\O.OC_6H_4.OH\end{matrix}\right.$, is formed by the incomplete reduction of quinone with sulphurous acid, and by the direct combination of quinone and hydroquinone. It is also produced by adding chlorine-water gradually to a solution of hydroquinone;—

$$C_6H_4\left\{\begin{matrix}OH\\OH\end{matrix}\right. + \begin{matrix}HO.C_6H_4.OH\\HO.C_6H_4.OH\end{matrix} + 2Cl_2 = C_6H_4\left\{\begin{matrix}O.OC_6H_4.OH\\O.OC_6H_4.OH\end{matrix}\right. + 4HCl$$

Quinhydrone crystallizes in smooth, long needles, possessing a splendid beetle green lustre, and a faint smell of quinone, and dissolving in hot water, with a brown colour. In cold water it is almost insoluble, and by boiling water it is resolved into hydroquinone and quinone, which volatilizes with the steam. By oxidation, it is readily converted into quinone, and by reduction into hydroquinone.

Phenoquinone $C_6H_4\left\{\begin{array}{l}O.OC_6H_5\\O.OC_6H_5\end{array}\right.$—This beautiful body is produced by boiling an aqueous solution of one part of pure phenol with two and a half parts of chromic acid. It readily volatilizes with steam, and is freely soluble in water. Ether dissolves it from its aqueous solution, and on evaporation it is left behind as a crystalline mass, which, by sublimation, yields long, splendid red needles, possessing a green metallic lustre, and a faint, pungent smell, and melting at 71°. Phenoquinone has also been obtained by the action of phenol upon quinone;—

$$2C_6H_4\left\{\begin{array}{l}O>\\O>\end{array}\right. + \begin{array}{l}HO.C_6H_5\\HO.C_6H_5\end{array} = C_6H_4\left\{\begin{array}{l}O.OC_6H_5\\O.OC_6H_5\end{array}\right. + C_6H_4\left\{\begin{array}{l}OH\\OH\end{array}\right.$$

Monochoroquinone $C_6H_3ClO_2''$ is obtained by the action of chlorine on quinone; it forms long, yellow needles, which, by the action of sulphurous acid, are converted into colourless *monochlorhydroquinone* $C_6H_3Cl(OH)_2$, a compound which is also produced by evaporating a solution of quinone in strong hydrochloric acid.

Dichloroquinone $C_6H_2Cl_2O_2''$ crystallizes in large yellow prisms; by the action of sulphurous acid, it yields, first, *hexachloroquinhydrone*, which, by further reduction, is converted into *dichlorohydroquinone*.

Trichloroquinone $C_6HCl_3O_2''$.—By adding a mixture of phenol and potassium chlorate to dilute hydrochloric acid, a reddish-yellow crystalline mass is obtained, consisting of a mixture of trichloroquinone and tetrachloroquinone. To separate them, they are reduced by means of sulphurous acid, and the chlorinated hydroquinones exhausted with boiling water, which only dissolves trichlorohydroquinone, which, by oxidation, is reconverted into trichloroquinone, crystallizing in large, thin, yellow plates, melting at 163°, and easily subliming.

Tetrachloroquinone, or Chloranil $C_6Cl_4O_2''$.—This body is produced (generally together with trichloroquinone) by the action of potassium chlorate and hydrochloric acid upon all substances which yield picric acid, when boiled with nitric acid.

It crystallizes in brilliant, golden-yellow scales, which are insoluble in water, slightly in cold and freely in hot alcohol, and sublime at a high temperature. It is a very stable compound, and not acted upon by concentrated sulphuric acid, nitric acid, and aqua regia. On heating it with phosphorus pentachloride, it is converted into *hexachlorobenzene* C_6Cl_6. By boiling it with a solution of sulphurous acid, it yields *tetrachlorohydroquinone* or *chlorohydranil*, small white plates, which are insoluble in water.

Chloranilic Acid $C_6.Cl_2O_2''\left\{\begin{array}{l}OH\\OH\end{array}\right.$—Chloranil dissolves in dilute warm potash-solution with a red colour, and on cooling purple needles of potassium chloranilate crystallize out—

$$C_6Cl_4O''_2 + 4KOH = C_6Cl_2O_2\left\{\begin{matrix}OK\\OK\end{matrix}\right. + 2KCl + 2H_2O$$

By decomposing this salt with sulphuric acid, chloranilic acid is obtained in small reddish-white plates, which, after drying, assume the colour of red lead, and dissolve in water with a violet colour.

Chloranilamic Acid $C_6Cl_2O''_2\left\{\begin{matrix}NH_2\\OH\end{matrix}\right.$.—The ammonium salt of this acid is obtained by dissolving choranil in ammonia. The free acid crystallizes in almost black needles, having a diamond-lustre. By heating it with dilute acids, it is converted into chloranilic acid.

Pyrocatechin, or Oxyphenic Acid $C_6H_4\left\{\begin{matrix}OH\\OH\end{matrix}\right.$.—This second dioxybenzene is found amongst the products of the distillation of wood, and in several vegetable extracts, such as "kino," "catechu," &c.; and has also been found, but in small quantity only, in the green leaves of the Virginian creeper. It is also produced by heating oxysalicylic acid:—

$$C_6H_3\left\{\begin{matrix}OH\\CO.OH\\OH\end{matrix}\right. = C_6H_4\left\{\begin{matrix}OH\\OH\end{matrix}\right. + CO_2$$

and by fusing metaphenolsulphonic acid or meta-iodophenol with potash.

Pyrocatechin is readily soluble in water and alcohol, and crystallizes in square prisms, melting at 112°, and boiling at 245°, but subliming at a lower temperature in shining plates. Its alkaline solution absorbs oxygen, and becomes dark-green, and then black. The aqueous solution of pyrocatechin gives, with lead acetate, a white precipitate $C_6H_4O_2Pb$, and assumes a green colour by adding ferric chloride.

Pyrocatechin-methyl Ether, or *Guaiacol* $C_6H_4\left\{\begin{matrix}OH\\OCH_3\end{matrix}\right.$, is found amongst the products of dry distillation of "guaiacum" and beechwood, and forms a chief constituent of the genuine or wood-tar creosote. It has been also produced artificially by heating pyrocatechin with caustic potash and potassium methylsulphate—

$$C_6H_4\left\{\begin{matrix}OK\\OK\end{matrix}\right. + \left.\begin{matrix}CH_3\\K\end{matrix}\right\}SO_4 = C_6H_4\left\{\begin{matrix}OCH_3\\OK\end{matrix}\right. + K_2SO_4$$

It is a colourless liquid, boiling at 205°, and possessing an aromatic smell. By heating it with concentrated hydriodic acid, it is resolved into methyl iodide and pyrocatechin.

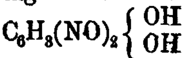
Resorcin $CH_4\left\{\begin{matrix}ON\\OH\end{matrix}\right.$.—This body is formed by fusing several resins or gum-resins (as galbanum), or extract of sapan-wood and other dye-woods, with caustic potash; and it has also been produced by the action of caustic potash upon benzenedisulphonic acid, paraphenolsulphonic acid, and para-iodophenol.

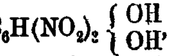
It forms colourless, triclinic crystals, melting at 99°, and boiling at 271°. It is very soluble in water, and possesses a sweetish and harsh taste. Its aqueous solution is coloured dark violet by ferric salts.

When a solution of nitrous acid in nitric acid is added to a cold and dilute etherial solution of resorcin, it is converted into *diazoresorcin* $C_{18}H_{12}N_2O_6$, dissolving in acetic acid with a dark cherry-red colour, and crystallizing in small granular crystals, having a green, metallic lustre.

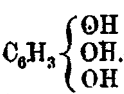
By the action of hot sulphuric acid, or hydrochloric acid, this compound is converted into *diazoresorufin* $C_{36}H_{18}N_4O_9$, separating from hot hydrochloric acid in small dark-red and brilliant granular crystals. It dissolves in alkalis with a crimson colour; the dilute solution exhibits a splendid vermilion-red fluorescence.

By heating diazoresorcin with acetyl chloride in sealed tubes, the compound $C_{48}H_{30}N_4Cl_8O_{15}$ is formed, crystallizing from acetic acid in yellow scales, and dissolving in alkalis with a splendid violet colour. Hot nitric acid converts it into the tetrazo-compound $C_{48}H_{18}N_{14}Cl_8O_{33}$, crystallizing in small purple plates, the etherial solution of which shows a really surprising vermilion-red fluorescence.

Mononitroresorcin  $C_6H_3(NO)_2\left\{\begin{matrix}OH\\OH\end{matrix}\right.$ is contained in considerable quantity in the mother-liquid from the preparation of diazoresorcin. It crystallizes in very thin and long, straw-coloured needles, and forms three series of salts, the colour of which is lemon-yellow, golden-yellow, and dark orange.

Trinitroresorcin, or Styphnic Acid  $C_6H(NO_2)_3\left\{\begin{matrix}OH\\OH\end{matrix}\right.$, is obtained by the action of nitric acid upon resorcin, and all resins and extracts which yield resorcin on fusion with potash. It crystallizes in pale-yellow hexagonal prisms, and possesses a very astringent taste. Its reddish-yellow salts crystallize well, and when heated explode even more violently than the picrates.

TRIOXYBENZENES.

Pyrogallol, or Pyrogallic Acid  $C_6H_3\left\{\begin{matrix}OH\\OH\\OH\end{matrix}\right.$.—This body is formed when gallic acid $C_6H_2(OH)_3CO_2H$ is heated to 200°. It crystallizes in shining white needles, and is readily soluble in water; the solution has no acid reaction, and colours ferrous salts dark-blue, and ferric salts red. By exposing an alkaline solution to the air, it rapidly absorbs oxygen, and assumes a dark colour; it is therefore used to absorb oxygen from a mixture of gases, but it is not adapted for a quantitative determination of oxygen, because there is always a small quantity of carbon monoxide formed at the same time. By boiling it with concentrated caustic potash, it is decomposed into acetic acid, oxalic acid, and carbon dioxide. The salts of silver, gold, &c., are reduced to the metallic state by pyrogallic acid.

By the action of acetyl chloride on pyrogallol, *triacetyl-pyrogallol* $C_6H_2(O.C_2H_3O)_3$ is obtained, a white crystalline solid; and by acting on pyrogallol with bromine, it yields *tribromopyrogallol* $C_6Br_3(OH)_3$, separating from alcohol in large colourless crystals.

Phloroglucin $C_6H_3\left\{\begin{matrix}OH\\OH\\OH\end{matrix}\right.$ is produced by fusing phloretin, quercitrin, or maclurin (see Glucosides) with caustic potash; and is also obtained by the same reaction from kino, dragon's-blood, gamboge, &c. It crystallizes from an aqueous solution in large rhombic prisms, containing two molecules of water, and possessing a sweet taste. The anhydrous compound melts at 220°, and sublimes, when heated more strongly. It forms deliquescent salts with alkalis, and reduces alkaline copper-solutions. Ferric chloride imparts to its aqueous solution a deep-violet colour. By treating it with acetyl chloride, it is converted into *triacetyl-phloroglucin* $C_6H_3(O.C_2H_3O)_3$, which crystallizes in small prisms. By adding bromine-water to an aqueous solution of phloroglucin, a precipitate of *tribromophloroglucin* $C_6Br_3(OH)_3$ is produced, which crystallizes in long needles. By the action of dilute nitric acid, it is converted into *nitrophloroglucin* $C_6H_2.NO_2(OH)_3$, crystallizing in small reddish-yellow plates. When phloroglucin is dissolved in ammonia, *phloramine* or *amidophloroglucin* $C_6H_3(NH_2)$-$(OH)_2$ is formed, which is not freely soluble in alcohol, and crystallizes in small thin plates, resembling mica; it is a base, forming crystalline salts.

Filicic Acid, or *Dibutyryl-phloroglucin* $C_6H_3\left\{\begin{matrix}OH\\OC_4H_7O\\OC_4H_7O\end{matrix}\right.$, occurs in the root of the male fern (*Aspidium Filix-mas*), and is deposited from the etherial extract of this root in crystals. On fusing it with caustic potash, it is resolved into butyric acid and phloroglucin.

METALLIC DERIVATIVES OF BENZENE.

Mercury-diphenyl $\left.\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\right\}Hg$ is formed by the action of sodium amalgam on bromobenzene. It is insoluble in water, and crystallizes from benzene in long colourless prisms, melting at 120°. A small quantity may be sublimed by heating it carefully; but on heating a larger quantity to above 300°, decomposition sets in; and benzene, diphenyl, carbonaceous matter, and free mercury are formed. By the action of acids, it is decomposed into benzene and a mercuric salt and when it is heated with iodine, according to the proportion of the two bodies present, either iodobenzene and *phenylmercuric iodide* $\left.\begin{matrix}C_6H_5\\I\end{matrix}\right\}Hg$ are formed, or iodobenzene and mercuric iodide.

Stannic-phenyl Triethide $\left.\begin{matrix}C_6H_5\\(C_2H_5)_3\end{matrix}\right\}Sn$ is obtained by the action of sodium upon a mixture of bromobenzene and triethyl-stannic iodide. It is a colourless, strongly refractive liquid, boiling at 254°; its vapour slowly absorbs oxygen. By the action of iodine, it is resolved into iodobenzene and triethyl-stannic iodide.

ADDITIVE COMPOUNDS OF BENZENE.

Benzene Hexachloride $C_6H_6Cl_6$ is obtained, by the action of chlorine on benzene, in the sunshine or at the boiling-point, in colourless crystals, melting at 157°, and boiling, with partial decomposition, at 288°. On heating it with alkalis, it is resolved into hydrochloric acid and trichlorobenzene.

A similar compound is *Benzene Hexabromide* $C_6H_2Br_6$.

Benzene Trichlorhydrin $C_6H_6(Cl_3)(OH)_3$ is formed by shaking benzene with aqueous hydrochlorous acid. It is slightly soluble in water, and freely in alcohol and benzene, and crystallizes at a low temperature in small plates, melting at 10°. By the action of a dilute solution of sodium carbonate, an amorphous deliquescent mass called *phenose* $C_6H_6(OH)_6$ is obtained, which, as well as the trichlorhydrin, yields, when heated with hydriodic acid, *moniodobenzolene* $C_6H_{11}I$, a heavy, colourless liquid, which boils without decomposition.

Trichlorophenomalic Acid $C_6H_6Cl_3O_5$ is produced, together with oxalic acid, chlorinated benzenes, and quinones, &c., by the action of moderately strong sulphuric acid and potassium chlorate on benzene. It crystallizes from a warm, aqueous solution in colourless plates. By boiling it with alkalis, it is decomposed with the formation of fumaric acid.

COMPOUNDS WITH SEVEN ATOMS OF CARBON.

METHYL-BENZENE OR TOLUENE $C_6H_5.CH_3$.

This hydrocarbon is found in the light oils from coal-tar and wood-tar, and also among the products of dry distillation of balsam of tolu, dragon's-blood, and other resins. It has been formed synthetically by adding sodium to a mixture of bromobenzene, methyl iodide, and pure anhydrous ether, and keeping the mixture cold. As soon as the action is over, the product is distilled, and the toluene isolated by fractional distillation. Pure toluene is also produced by distilling the isomeric acids $C_6H_4(CH_3)CO_2H$, and similar acids, with lime.

Toluene is a limpid liquid, boiling at 111°, and smelling like benzene. It has the specific gravity 0·88 at 0°, and does not solidify at – 20°. On oxidation it yields benzoic acid.

SUBSTITUTION-PRODUCTS OF TOLUENE.

When chlorine is passed into toluene, and the liquid is kept cold during the action, or when chlorine acts on the hydrocarbon in the presence of iodine, only the hydrogen in the aromatic nucleus is replaced, whilst the action of pure chlorine on the boiling hydrocarbon produces only substitution in the methyl-group.

The chlorine in these latter compounds is easily replaceable by other elements or radicals, whilst the substitution-products containing the chlorine in the aromatic nucleus are as stable bodies as the chlorobenzenes.

By treating any of the products thus obtained with chlorine and iodine, further substitution takes place only in the aromatic group; but by acting on the boiling compounds with pure chlorine, only the hydrogen of the methyl is replaced.

By means of these reactions the following substitution-products have been obtained, to which are added some isomerides, which have been formed by other reactions, and stand in the second or third line. The numbers affixed to these compounds indicate the position of the chlorine (see page 314).

	Toluene or Methyl-benzene. $C_6H_5.CH_3$	Benzyl Chloride. $C_6H_5.CH_2Cl$	Benzylene Dichloride. $C_6H_5.CHCl_2$	Benzenyl Trichloride. $C_6H_5.CCl_3$
Boiling-point .	111°	176°	205°	214°
	Monochlorotoluene. $C_6HCl.CH_3$	Chlorobenzyl Chloride. $C_6H_4Cl.CH_2Cl$	Chlorobenzylene Dichloride. $C_6H_4Cl.CHCl_2$	Chlorobenzenyl Trichloride. $C_6H_4Cl.CCl_3$
Boiling-point . .	1·4 = 157° 1·3 = 156 —	214° — —	1·4 = 234° 1·2 = 229 —	1·4 = 245° 1·3 = 235 1·2 = 260
	Dichlorotoluene. $C_6H_3Cl_2.CH_3$	Dichlorobenzyl Chloride. $C_6H_3Cl_2.CH_2Cl$	Dichlorobenzylene Dichloride. $C_6H_3Cl_2.CHCl_2$	Dichlorobenzenyl Trichloride. $C_6H_3Cl_2.CCl_3$
Boiling-point . .	196°	241°	257°	273°
	Trichlorotoluene. $C_6H_2Cl_3.CH_3$	Trichlorobenzyl Chloride. $C_6H_2Cl_3.CH_2.Cl$	Trichlorobenzylene Dichloride. $C_6H_2Cl_3.CH.Cl_2$	Trichlorobenzenyl Trichloride. $C_6H_2Cl_3.CCl_3$
Boiling-point . .	235°	273°	281°	308°
Melting-point . .	76	—	—	82
	Tetrachlorotoluene. $C_6HCl_4.CH_3$	Tetrachlorobenzyl Chloride. $C_6HCl_4.CH_2Cl$	Tetrachlorobenzylene Dichloride. $C_6HCl_4.CHCl_2$	Tetrachlorobenzenyl Trichloride. $C_6H_4Cl_4.CCl_3$
Boiling-point . .	271°	296°	306°	306°
Melting-point . .	92	—	—	104
	Pentachlorotoluene. $C_6Cl_5.CH_3$	Pentachlorobenzyl Chloride. $C_6Cl_5.CH_2Cl$	Pentachlorobenzylene Dichloride. $C_6Cl_5.CHCl_2$	
Boiling-point . .	301°	326°	334°	
Melting-point . .	218	103	109	

More than seven atoms of chlorine cannot be introduced into toluene, as, by the further action of chlorine upon the last substitution-products, the molecule is decomposed with the formation of hexachlorobenzene.

1·4 *Monochlorotoluene* is formed by the direct action of chlorine upon toluene, and the isomeric 1·3 compound has been obtained from toluidine, which is first converted into acetoluide, and the latter treated by chlorine. The chlorinated compound yields, on boiling with alkalis, monochlortoluidine, which is converted into a diazo-compound and the latter decomposed by absolute alcohol:—

$$C_6H_3Cl\left\{\begin{matrix}CH_3\\N_2.SO_4H\end{matrix}\right. + C_2H_5.OH = C_6H_4Cl.CH_3 + N_2 + H_2SO_4 + C_2H_4O$$

When bromine-vapour is passed into boiling toluene, substitution takes place only in the methyl group, and the first product formed is *benzyl bromide* $C_6H_5.CH_2Cl$, but by acting with bromine on toluene in the cold two isomeric bromotoluenes are produced.

1·4 *Bromotoluene* forms rhombic, colourless crystals, melting at 28·5°, and boiling at 181°.

1·3 *Bromotoluene* is a liquid which does not crystallize at a low temperature, and boils at 181°.

By the further action of bromine on toluene in the cold, *dibromotoluene* $C_6H_3Br_2.CH_3$ is obtained, a crystalline solid, melting at 180°, and boiling at 245°.

Iodine substitution-products of toluene have been obtained from the three isomeric amidotoluenes by converting them into diazo-compounds, and decomposing the latter with hydriodic acid.

1·2 *Iodotoluene* and 1·3 *Iodotoluene* are liquids, both boiling at 204°, whilst 1·4 *Iodotoluene* crystallizes in shining, thin plates, melting at 35°, and boiling at 211°·5.

NITRO-SUBSTITUTION-PRODUCTS.

Nitrotoluenes $C_6H_4(NO_2)CH_3$.—By dissolving toluene in fuming nitric acid, and adding water to the solution, a heavy oily liquid, resembling nitrobenzene, is obtained, which is a mixture of two isomerides; they may be separated by continued fractional distillation.

1·4 *Nitrotoluene* crystallizes in colourless prisms, melting at 54°, and boiling at 237°. By oxidizing it with dilute nitric acid, it is converted into paranitrobenzoic acid.

1·2 *Nitrotoluene* is a liquid which does not solidify in a freezing mixture, and boils at 223°; boiling dilute nitric acid has hardly any action on it.

1·3 *Nitrotoluene* has been produced by converting 1·4 amidotoluene into a nitro-amidotoluene, which was transformed into a diazo-compound, and the latter decomposed by alcohol. It forms colourless crystals, melting at 16°, and boiling at 227°. Dilute nitric acid oxidizes it to common nitrobenzoic acid.

Dinitrotoluene $C_6H_3(NO_2)_2CH_3$ exists in two forms. One of them is produced by the action of hot concentrated nitric acid on toluene, 1·4 nitrotoluene, or 1·2 nitrotoluene. It crystallizes from alcohol in long, colourless, brittle needles, melting at 71°. The second form is obtained by the action of concentrated nitric acid on 1·3 nitrotoluene; it forms long, yellow needles, melting at 60°.

Trinitrotoluene $C_6H_2(NO_2)_3CH_3$ is formed by boiling toluene for some days with a mixture of fuming sulphuric and nitric acids. It is sparingly soluble in alcohol, and forms long needles at 82°. By treating 1·3 nitrotoluene in the same way, another *trinitrotoluene* is obtained, crystallizing as carbon sulphide in small plates, melting at about 82°.

AMIDOTOLUENES.

Toluidine or 1·4 *Amidotoluene* $C_6H_4\left\{\begin{matrix}CH_3\\NH_2\end{matrix}\right.$ is formed by the reduction of the corresponding nitrotoluene, and has also been produced from methyl-aniline; by heating the hydrochloride of the latter base to 335° (the melting-point of lead), it undergoes a molecular change, and is converted into toluidine hydrochloride. It crystallizes from aqueous alcohol in large transparent, shining plates, melting at 45°, and boiling at 202°. It possesses a peculiar odour, and is sparingly soluble in water; its aqueous solution is coloured brown by a solution of bleaching-powder. Toluidine has in its reactions the greatest resemblance to aniline, and forms salts, most of which crystallize well. The most characteristic is the oxalate, which is but sparingly soluble in water and alcohol, and insoluble in ether.

Pseudotoluidine or 1·2 *Amidotoluene* is formed by the reduction of the corresponding nitrotoluene. It is a colourless liquid, remaining fluid at − 20°, and boiling at 198°. Its aqueous solution is coloured blue by bleaching-powder, and its oxalate is freely soluble in water, alcohol, and ether.

The commercial toluidine and heavy aniline are mixtures of the two toluidines and aniline. To separate the three bases, they are converted into oxalates, which are crystallized from hot water. Toluidine oxalate, which crystallizes first, is purified by recrystallization, and decomposed by soda-solution. The mother-liquor is evaporated to dryness, the residue exhausted with ether, the etherial solution evaporated, and the residue treated with soda-solution; and thus pure pseudotoluidine is obtained.

Pseudotoluidine has also been produced from 1·4 bromotoluene, which, by the action of concentrated nitric acid, yields two isomeric nitrobromotoluenes; one being a liquid, is present in a smaller quantity than the solid one. By reducing the latter, an amidobromotoluene is formed, which, by the action of water and sodium-amalgam, is converted into pseudotoluidine.

1·3 *Amidotoluene* is produced by reducing 1·3 nitrotoluene; it is a liquid boiling at 197°, and giving, with bleaching-powder solution, a blue colour, like pseudotoluidine.

The three amidotoluenes yield three acetoluides $C_6H_4\left\{\begin{matrix}CH_3\\NH.CO.CH_3\end{matrix}\right.$ differing from each other by their solubilities in water:—

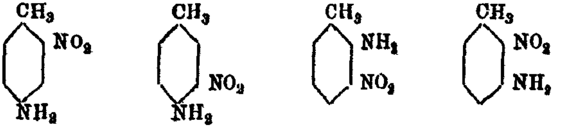
1,000 parts of water dissolve at	22°	0·89	parts of	1·4	Acetoluide.
" " "	19	8·6	"	1·3	
" " "	14	4·4	"	1·2	

Nitro-amidotoluene $C_6H_3.CH_3\left\{\begin{matrix}NH_2\\NO_2\end{matrix}\right.$.—This compound exists in four modifications. The first is obtained by reducing the dinitrotoluene, melting at 71° with ammonium sulphide; it melts at 77°·5, and forms crystalline salts. By converting it into a diazo-compound, and decomposing this with absolute alcohol, 1·2 nitrotoluene is formed.

The three other modifications have been prepared by nitrating the three isomeric acetoluides, and decomposing the product with alkalis. 1·4 toluidine yields a nitrotoluidine, melting at 114°; it does not combine with acids, and its diazo-compound yields 1·3 nitrotoluene. The nitrotoluidine from 1·2 toluidine forms yellow needles, melting at 128°, and is but a feeble base; by the action of nitrous acid and alcohol it is converted into 1·3 nitrotoluene. The fourth modification of nitro-amidotoluene is obtained from 1·3 toluidine; it crystallizes in dark-yellow needles, melting at 134°, and forms unstable salts; its diazo-compound is readily converted into 1·2 nitrotoluene.

The constitution of these four nitrotoluidines is shown by the following formulæ:—

Melting-point 77°·5 114° 128° 134°



DIAMIDOTOLUENES $C_6H_3.CH_3\left\{\begin{matrix}NH_2\\NH_2\end{matrix}\right.$.

We know three compounds having this composition. 2·4 *diamidotoluene* is obtained by reducing the dinitrotoluene, melting at 71° with tin, and hydrochloric acid. It forms long, colourless needles, melting at 99°, and boiling at 280°. 3·4 *diamidotoluene* is formed by reducing the nitrotoluidine, melting at 114°; it crystallizes in scales, melting at 88°·5, and boiling at 265°. Nitrotoluidine, melting at 128°, yields 2·3 *diamidotoluene*, a crystalline body, melting at about 80°, and boiling at 270°; it readily absorbs oxygen, and assumes a blue colour.

By the action of ammonium sulphide on trinitrotoluene, two amido-compounds are formed; *dinitroamidotoluene* $C_6H_2(CH_3)\left\{\begin{matrix}(NO_2)_2\\NH_2\end{matrix}\right.$ which crystallizes in small yellow needles, melting at 168°, and *nitrodiamidotoluene* $C_6H_2(CH_3)\left\{\begin{matrix}NO_2\\(NH_2)_2\end{matrix}\right.$, small red prisms melting at 132°.

OXYTOLUENES.

Cresol $C_6H_4\left\{\begin{matrix}OH\\CH_3\end{matrix}\right.$.—The cresol contained in coal-tar consists chiefly of *paracresol* or 1·4 *cresol*.

The pure compound is most conveniently prepared by converting solid toluidine into diazotoluene sulphate, and decomposing the latter with water. It crystallizes in white needles, melting at 35°·5, boiling at 200°, and smelling like phenol. The same compound is also obtained by fusing 1·4 toluenesulphonic acid with caustic potash; this sulpho-acid is formed together with the 1·2 acid by dissolving toluene in sulphuric acid.

Cresol-methyl Ether $C_6H_4\left\{\begin{matrix}CH_3\\OCH_3\end{matrix}\right.$ is obtained by heating the potassium compound of 1·4 cresol with methyl iodide. It is a liquid possessing an aromatic odour, and boiling at 174°.

Metacresol, or 1·2 *cresol*, is produced by the action of caustic potash upon 1·2 toluenesulphonic acid. It is a liquid boiling at 190°.

Orthocresol, or 1·3 *Cresol*, has been obtained from *thymol* $C_6H_3\left\{\begin{matrix}OH\\CH_3\\C_3H_7\end{matrix}\right.$, a compound to be described afterwards. By heating it with phosphorus pentoxide it is resolved into propylene, and orthocresol, a colourless liquid, boiling at about 200°.

Dinitrocresol $C_6H_2(NO)_2\left\{\begin{matrix}OH_3\\OH\end{matrix}\right.$ is produced by the action of nitrous acid upon solid toluidine; it forms yellow crystals, melting at 84°.

An isomeric compound is contained in the so-called "Victoria-yellow," or "aniline-orange." This colouring matter, of unknown origin, consists principally of the sodium salt of a dinitrocresol, which crystallizes in pale-yellow needles, melting at 190°.

Trinitrocresol $C_6H_2(NO_2)_3OH$ has great resemblance to picric acid, but is much less soluble in water, and may therefore easily be obtained in the pure state by boiling commercial cresol (containing phenol) with nitric acid.

DIOXYTOLUENES.

Homopyrocatechin and Creosote.—The *genuine* or *wood-tar creosote* is obtained from the products of dry distillation of beech-wood, and is a mixture containing phenol, cresol, phlorol $C_6H_3(CH_3)_2OH$, guaiacol (page 342), and *creosol* $C_6H_3(CH_3)\left\{\begin{matrix}OH\\OCH_3\end{matrix}\right.$. Creosol is a liquid boiling at 219°, and possessing an aromatic odour; by heating it with concentrated hydriodic acid, it yields methyl iodide, and *homopyrocatechin* $C_6H_3(CH_3)\left\{\begin{matrix}OH\\OH\end{matrix}\right.$, which forms a syrupy liquid.

Orcin $C_6H_3(CH_3)\left\{\begin{matrix}OH\\OH\end{matrix}\right.$.—All the lichens (species of *Rocella* and *Lecanora*) which are used in the preparation of archil and litmus contain either free orcin, or certain acids, and compound ethers, which, under the influence of heat or alkalis, yield orcin:—

$$\underset{\text{Orsellinic Acid.}}{C_6H_2(CH_3)(OH)_2CO_2H} = C_6H_3(CH_3)(OH)_2 + CO_2$$

$$\overset{\text{Erythrin.}}{\left.\begin{matrix}C_6H_2(CH_3)(OH)_2CO.O\\C_6H_2(CH_3)(OH)_2CO.O\end{matrix}\right\}} C_4H_6(OH)_2 + 2H_2O =$$

$$\overset{\text{Orsellinic Acid.}}{2C_6H_2(CH_3)(OH)_2CO_2H} + \overset{\text{Erythrite.}}{C_4H_6(OH)_4}$$

$$\overset{\text{Picroerythrite.}}{\left.\begin{matrix}C_6H_2(CH_3)(OH)_2CO\\C_6H_4(OH)_3\end{matrix}\right\}}O + H_2O = C_6H_2(CH_3)(OH)_2CO_2H + C_4H_6(OH)_4$$

To prepare orcin, the lichens are macerated with milk of lime, and the filtrate precipitated with hydrochloric acid. The precipitate, after being washed with water, is boiled with milk of lime in a flask provided with a long neck, and the liquid, after filtration, freed from the lime by carbon dioxide. The solution is then evaporated to dryness, and the residue exhausted with benzene, which dissolves orcin, and leaves impure erythrite behind.

Orcin has also been produced by dissolving monochlorotoluene in warm concentrated sulphuric acid, and converting the two isomeric sulphonic acids, which thus are formed, into the barium salts, which are easily separated by re-crystallization, one being readily soluble in water, and the other not. On converting the latter into potassium salt, and fusing this with potash, orcin is formed:—

$$C_6H_3(CH_3)\left\{\begin{matrix}Cl\\SO_3K\end{matrix}\right. + 2KOH = C_6H_3(CH_3)\left\{\begin{matrix}OH\\OH\end{matrix}\right. + KCl + K_2SO_3$$

Orcin is also produced together with para-oxybenzoic acid, when aloes is fused with caustic potash.

Orcin crystallizes from water in monoclinic prisms containing one molecule of water, and melting at 58°. The anhydrous compound melts at 86°, and boils at 290°. It has an intense sweet, but nauseous taste, and dissolves in water, alcohol, ether, and chloroform; its aqueous solution gives with ferric chloride a deep violet colour.

Orcin forms readily metallic compounds, and decomposes, in the fused state, sodium carbonate. On passing the vapour of nitric acid containing nitrous acid over it, it assumes first a brown colour, and afterwards becomes intense red; the product thus formed dyes on wool and silk a fine red shade. With a solution of bleaching-powder it gives a violet colour, which soon disappears; its alkaline solutions absorb readily oxygen, and become brown or red.

Orcin combines also with dry ammonia forming a deliquescent compound, which, when exposed to the air, is converted into *orcein* $C_7H_7NO_3$:—

$$C_7H_8O_2 + NH_3 + O_2 = C_7H_7NO_3 + 2H_2O$$

Orcein is an amorphous red powder, which is sparingly soluble in water, and more freely in alcohol with a scarlet colour. In alkalis it dissolves with a purple colour; this solution is precipitated by many metallic salts, red or purple lakes being formed.

Orcein is the colouring-matter of *Archil*, which is prepared by treating the lichens with hot aqueous ammonia in presence of air.

The same lichens are used for preparing *Litmus*, which is generally obtained from *Lecanora tartarea* by steeping it in urine, and adding lime and potassium carbonate. The mixture is exposed to the air, and frequently stirred up; after a few weeks, a blue solution is formed, which is thickened with chalk or gypsum, and formed in small cakes.

The colouring-matter of litmus is probably a product of oxidation of orcein; it has been obtained pure by adding soda-crystals to an ammoniacal solution of orcein, and exposing the liquid to the air at a temperature of 60° to 80°. On adding hydrochloric acid to the blue solution, the colouring-matter is precipitated in red flakes; it is not freely soluble in water, forming a pale-red solution, which becomes blue by adding an alkali. Litmus contains, therefore, a weak acid, forming salts having a blue colour; the commercial product contains the potassium salt.

Trichlorotoluquinone $C_6Cl_3(CH_3)\left\{\begin{matrix}O\\O\end{matrix}\right>$ is obtained by treating cresol from coal-tar with dilute hydrochloric acid and potassium chlorate. It is sparingly soluble in cold and freely in hot alcohol, and crystallizes in pale-yellow scales. Sulphurous acid converts it into *trichlorotoluhydroquinone* $C_6Cl_3(CH_3)(OH)_2$, forming small white needles, which by oxidation are readily reconverted into the quinone.

BENZYL COMPOUNDS.

The radical *Benzyl* is contained in a series of compounds which in many reactions exhibit the closest analogy with the compounds of the monad alcohol-radicals. They differ, however, from the latter by containing the aromatic nucleus, and forming, therefore, also products of substitution, corresponding to the derivatives of benzene.

Benzyl Chloride $C_7H_5.CH_2Cl$ is easily obtained by passing the required quantity of chlorine into boiling toluene, and purifying the product by fractional distillation. It is a limpid, refractive liquid, boiling at 176°.

Benzyl Bromide $C_6H_5.CH_2Br$ is produced by the action of bromine on boiling toluene. It boils at 199°, and possesses an irritating odour.

Benzyl Iodide $C_6H_5.CH_2I$.—To prepare this compound, one part of benzyl chloride is mixed with five parts of concentrated hydriodic acid, and the mixture kept in the dark for three weeks, and frequently shaken. Pure benzyl iodide is a white crystalline solid, melting at 24°; it cannot be distilled, and decomposes at 240°. Its odour is very irritating, and produces a copious flow of tears.

Benzyl Alcohol $C_6H_5.CH_2OH$ was first produced by treating its aldehyde (oil of bitter almonds) with alcoholic potash, which acts violently upon it, half of the aldehyde being reduced to the alcohol, and the other half oxidized to benzoic acid:—

$$2C_6H_5.COH + KOH = C_6H_5.CH_2.OH + C_6H_5.CO.OK$$

Benzyl alcohol is also formed by acting with nascent hydrogen on the aldehyde or benzoic acid, and may be prepared by adding sodium amalgam gradually to a boiling solution of benzoic acid. It has also been produced by decomposing the acetate with caustic potash.

Benzyl alcohol is a liquid boiling at 207°, and possessing an aromatic odour. Oxidizing agents convert it into benzaldehyde and benzoic acid, and the hydracids of the chlorine-group transform it into the corresponding haloid-ethers. On distillation with concentrated potash-solution, it yields toluene and benzoic acid:—

$$2C_6H_5.CH_2.OH = C_6H_5.CH_3 + C_6H_5.CO.OH$$

Dibenzyl Ether $\left.\begin{matrix}C_6H_5.CH_2\\C_6H_5.CH_2\end{matrix}\right\}O$ has been prepared by heating the alcohol with fused boron trioxide; it is an oily liquid, boiling above 300°.

Benzyl Acetate $\left.\begin{matrix}C_6H_5.CH_2\\CH_3.CO\end{matrix}\right\}O$ is readily produced by heating the chloride or bromide with potassium or silver acetate, or by the action of sulphuric acid on a mixture of acetic acid and benzyl alcohol. It is an oily liquid, which possesses an agreeable odour, and boils at 210°.

Benzyl Hydrosulphide, or *Benzyl Mercaptan*, $C_6H_5.CH_2.SH$, is a colourless strongly refractive liquid, which is formed by acting with alcoholic potassium hydrosulphide on benzyl chloride. It possesses a strong alliaceous odour, and boils at 195°. With mercuric oxide it forms the crystalline mercaptide $(C_6H_5.CH_2S)_2Hg$.

Benzyl Sulphide $\left.\begin{matrix}C_6H_5.CH_2\\C_6H_5.CH_2\end{matrix}\right\}S$ is formed by treating the chloride with an alcoholic solution of potassium sulphide. It crystallizes in white needles, melting at 49°, and decomposing at a higher temperature. Nitric acid oxidizes it to *benzyl sulphoxide* $(C_6H_5.CH_2)_2SO$.

Benzyl Disulphide $\left.\begin{matrix}C_6H_5.CH_2S\\C_6H_5.CH_2S\end{matrix}\right\}$ is formed by exposing the hydrosulphide to the air; it crystallizes in colourless scales. Nascent hydrogen converts it again into the mercaptan.

NITROGEN BASES OF BENZYL.

These bases are formed by heating benzyl chloride with alcoholic ammonia. The hydrochlorides thus obtained can be easily separated; that of benzylamine being freely soluble in water, whilst the salt of the diamine is but sparingly soluble in cold, but readily in hot water, and that of the triamine almost insoluble.

Benzylamine $C_6H_5.CH_2.NH_2$ is a colourless, strongly alkaline liquid boiling at 185°. It is soluble in water, absorbs carbon dioxide from the air, and neutralizes acids, forming crystalline salt. The pure compound is also readily obtained by heating benzyl chloride with silver cyanate, and distilling the product with potash.

Dibenzylamine $(C_6H_5.CH_2)_2NH$ is a thick oily liquid, which is insoluble in water, and distils at a high temperature without decomposition.

Tribenzylamine $(C_6H_5.CH_2)_3N$ forms colourless needles, which are insoluble in water, but dissolve in hot alcohol. It melts at 91°, and boils above 300°. On heating it in a current of gaseous hydrochloric acid, it is resolved into benzyl chloride, and dibenzylamine hydrochloride.

$$\left.\begin{matrix}C_6H_5.CH_2\\C_6H_5.CH_2\\C_6H_5.CH_2\end{matrix}\right\}N + 2HCl = C_6H_5.CH_2Cl + \left.\begin{matrix}C_6H_5.CH_2\\C_6H_5.CH_2\\H\end{matrix}\right\}N.HCl$$

Benzyl Carbimide $\left.\begin{matrix}C_6H_5.CH_2\\CO\end{matrix}\right\}N$.—This compound, commonly called *benzyl cyanate*, is obtained by distilling the chloride with silver cyanate. It is a colourless liquid, boiling at 200°. It is easily transformed by heat into the polymeric *benzyl isocyanurate* $(C_6H_5.CH_2)_3(CON)_3$, which compound, therefore, is the chief product of the above reaction; it crystallizes from alcohol in very light, silky needles, melting at 157° and boiling at 320°.

Benzyl-Urea $CO\left\{\begin{matrix}NH_2\\NH(C_6H_5.CH_2)\end{matrix}\right.$ is produced by acting on the cyanate with alcoholic ammonia. It forms white needles, melting at 144°. It does not combine with nitric acid, but yields with hydrochloric acid and platinum chloride an insoluble precipitate.

Dibenzyl-Urea $CO\left\{\begin{matrix}NH(C_6H_5.CH_2)\\NH(C_6H_5.CH_2)\end{matrix}\right.$ is formed, together with carbon dioxide, by heating the isocyanurate with water in sealed tubes, or by heating benzyl-urea:—

$$2CO\left\{\begin{matrix}NH_2\\NH(C_6H_5.CH_2)\end{matrix}\right. = CO\left\{\begin{matrix}NH(C_6H_5.CH_2)\\NH(C_6H_5.CH_2)\end{matrix}\right. + CO\left\{\begin{matrix}NH_2\\NH_2\end{matrix}\right.$$

It crystallizes from alcohol in white needles, melting at 167°.

Benzyl Sulphocarbimide, or *Benzyl Mustard-oil* $\left.\begin{matrix}C_6H_5.CH_2\\CS\end{matrix}\right\}N$. When benzylamine is dissolved in carbon disulphide, it combines with it, forming *benzyl-sulphocarbamic acid*; on heating this compound with alcohol and mercuric chloride, it yields benzyl mustard-oil:—

$$CS\left\{\begin{matrix}N\left\{\begin{matrix}CH_2.C_6H_5\\H\end{matrix}\right.\\SH\end{matrix}\right. + HgCl_2 = N\left\{\begin{matrix}CH_2.C_6H_5\\CS\end{matrix}\right. + HgS + 2\,HCl$$

It is a crystalline solid, melting at 243°, and smelling like water-cress. This compound is isomeric with *tolyl mustard-oil* $N\left\{\begin{matrix}C_6H_4.CH_3\\CS\end{matrix}\right.$ which has been obtained by an analogous reaction from solid toluidine. Tolyl mustard-oil forms large pointed prisms, melting at 26°, boiling at 237°, and smelling like the oil of anise-seed.

PHOSPHORUS BASES OF BENZYL.

The monophosphine and diphosphine are formed together by heating benzyl chloride with phosphonium iodide and zinc oxide to 160°. The two compounds are separated, like the corresponding methyl bases (see page 96).

Benzylphosphine $C_6H_5.CH_2.NH_2$ is a colourless, very refractive liquid, boiling at 180°, and possessing a very peculiar and persistent odour. When exposed to the air, it absorbs oxygen so rapidly, that the temperature rises to above 100°, and thick white fumes are formed. The hydriodide crystallizes in long white needles, and is readily decomposed by water.

Dibenzylphosphine $(C_6H_5.CH_2)_2NH$ crystallizes from hot alcohol in glistening, stellate needles, having neither taste nor smell.

SUBSTITUTED BENZYL COMPOUNDS.

Chlorobenzyl Alcohol $C_6H_4Cl.CH_2.OH$.—To prepare this compound, silver acetate is heated with chlorobenzyl chloride (see page 347), and the acetate thus formed acted upon by ammonia. The alcohol forms long needles, melting at 66°; oxidizing agents convert it into chlorodracylic or 1·4 chlorobenzoic acid.

Dichlorobenzyl Alcohol $C_6H_3Cl_2.CH_2.OH$ has been obtained from dichlorobenzyl chloride; it crystallizes in needles melting at 77°.

Nitrobenzyl Alcohol $C_6H_4(NO_2)CH_2.OH$ is produced together with nitrobenzoic acid by acting with alcoholic potash on nitrobenzaldehyde. It is a thick, oily liquid, which is decomposed by heat.

Paranitrobenzyl Alcohol is prepared by dissolving benzyl acetate in fuming nitric acid, and heating the nitro-compound with ammonia. It crystallizes from hot water in colourless needles, melting at 93°, and yields on oxidation paranitrobenzoic acid.

Nitrobenzyl Hydrosulphide $C_6H_4(NO_2)CH_2.SH$.—This mercaptan is obtained by treating nitrobenzyl chloride with alcoholic ammonium sulphide, or boiling potassium hydrosulphide. It crystallizes from alcohol in small glistening plates, melting at 140°.

BENZOYL COMPOUNDS.

Benzonitrile $C_6H_5.CN$.—This compound has been produced by different reactions:—

(1.) By distilling a mixture of potassium cyanide and potassium benzenesulphonate:—

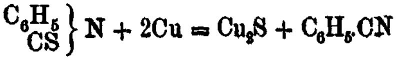
$$C_6H_5.SO_3K + KCN = C_6H_5.CN + SO_3K_2$$

(2.) By heating ammonium benzoate $C_6H_5.CO.ONH_4$, or benzamide $C_6H_5.CO.NH_2$, with phosphorus pentoxide.

(3.) By heating the isomeric phenyl carbamine or cyanobenzene for three hours to 220°:—

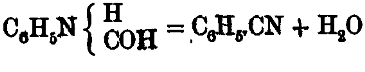
$$C_6H_5.NC = C_6H_5.CN$$

It is therefore also formed when phenyl mustard-oil is heated with finely-divided copper:—



$$\left.\begin{matrix}C_6H_5\\CS\end{matrix}\right\}N + 2Cu = Cu_2S + C_6H_5.CN$$

and further, it is obtained by distilling formanilide with strong hydrochloric acid:—



$$C_6H_5N\left\{\begin{matrix}H\\COH\end{matrix}\right. = C_6H_5.CN + H_2O$$

In these two last reactions the carbamine is first formed, but under the influence of heat converted into the more stable nitrile.

Benzonitrile is a colourless, oily, and refractive liquid, boiling at 191°, and smelling like bitter almonds. On heating it with alcoholic potash, it yields ammonia and potassium benzoate, and nascent hydrogen converts it into benzylamine:—

$$C_6H_5.CN + 2H_2 = C_6H_5.CH_2.NH_2$$

Nitrobenzonitrile $C_6H_4(NO_2)CN$ is obtained by dissolving the nitrile in fuming nitric acid. It crystallizes in white needles; reducing agents convert it into *amidobenzonitrile* $C_6H_4(NH_2)CN$, crystallizing in long prisms, melting at 52°, and boiling at 290°. This base forms crystalline salts; by heating it with strong hydrochloric acid, it yields ammonium chloride and amidobenzoic acid.

Benzaldehyde $C_6H_5.COH$ is the chief constituent of oil of bitter almonds. This oil does not exist in the free state in these seeds, but as glucoside called *amygdalin*, which, under the influence of a ferment, is resolved into benzaldehyde, prussic acid, and glucose (see Glucosides). Benzaldehyde is also formed by oxidizing benzyl alcohol, and by distilling a mixture of calcium benzoate and formate:—

$$C_6H_5.CO.OH + CHO.OH = C_6H_5.COH + CO_2 + H_2O$$

Another reaction by which this aldehyde is produced consists in passing the vapour of benzoic acid over heated zinc-dust:—

$$C_6H_5.CO.OH + Zn = C_6H_5.COH + ZnO$$

To obtain the pure aldehyde from oil of bitter almonds, it is shaken with a cold saturated solution of acid sodium sulphite; the compound $C_6H_5.CH\left\{\begin{matrix}OH\\SO_3Na\end{matrix}\right.$ being formed, which separates out in crystals. After being washed with cold alcohol, to remove prussic acid, the compound is decomposed by distilling it with a solution of sodium carbonate.

Pure benzaldehyde is a limpid and very refractive liquid, possessing a very characteristic smell, and boiling at 180°. It readily absorbs oxygen, being converted into benzoic acid; this oxidation takes place quickly by heating it with dilute nitric acid, whilst fuming nitric acid forms *nitrobenzaldehyde* $C_6H_4(NO_2)COH$, a crystalline solid, which volatilizes on heating.

When benzaldehyde is distilled with phosphorus pentachloride, it yields *benzylene dichloride* $C_6H_5.CHCl_2$, a colourless liquid boiling at 215°. The same compound is produced by the further action of chlorine on boiling benzyl chloride. It may be reconverted into the aldehyde by heating it with caustic potash or mercuric oxide:—

$$C_6H_5.CHCl_2 + HgO = C_6H_5.CHO + HgCl_2$$

By means of these reactions, artificial oil of bitter almonds is now manufactured from toluene.

Sulphobenzaldehyde $C_6H_5.CHS$ forms colourless crystals melting at 70°; it is prepared by heating benzylene dichloride with an alcoholic solution of potassium sulphide.

Hydrobenzamide, or *Benzylenediamine* $\left.\begin{array}{l} C_6H_5.CH \\ C_6H_5.CH \\ C_6H_5.CH \end{array}\right\} \begin{array}{l} N \\ N \end{array}$, is produced by leaving benzaldehyde or its chloride in contact with aqueous ammonia; it crystallizes in octahedrons, and is resolved by boiling water into benzaldehyde and ammonia.

Amarine $C_{21}H_{18}N_2$.—This isomeride of hydrobenzamide is obtained by the action of heat on the latter compound; and is also produced by passing ammonia into an alcoholic solution of benzaldehyde. Amarine crystallizes in glittering prisms melting at 100°; it has poisonous properties, and is a base forming sparingly soluble salts.

Lophine $C_{21}H_{16}N_2$ is formed by distilling hydrobenzamide or amarine; it is a base, crystallizing in long needles, melting at 270°.

When potassium cyanide is added to an alcoholic solution of benzaldehyde, or crude oil of bitter almonds (containing prussic acid) is mixed with alcoholic potash, the aldehyde is converted into *benzoin* $C_{14}H_{12}O_2$, a compound which is a derivative of the radical *stilbene* $C_{14}H_{12}$, and will be described afterwards.

BENZOIC ACID, OR PHENYLFORMIC ACID $C_6H_5.CO.OH$.

This acid occurs in *gum Benzoin* (from *Styrax benzoin*), and is sometimes found in the urine of herbivora, which always contains hippuric or benzamidacetic acid. Benzoic also exists as glucoside, called populin, in the bark and leaves of the aspen. It has been produced artificially by several reactions.

(1.) All aromatic hydrocarbons containing only one alcohol-radical are converted by oxidation with dilute nitric acid or chromic acid into benzoic acid. It is also formed by oxidizing benzyl alcohol, benzaldehyde, phenylacetic acid $C_6H_5.CH_2.CO_2H$, cinnamic acid $C_6H_5.C_2H_2.CO_2H$ and similar acids, and occurs among the products of oxidation of albuminous substances.

(2.) Sodium benzoate is formed by passing carbon dioxide into a mixture of bromobenzene and sodium:—

$$C_6H_5.Br + CO_2 + Na_2 = C_6H_5.CO_2Na + NaBr$$

(3.) By treating the same mixture with ethyl chlorocarbonate, it yields ethyl benzoate:—

$$C_6H_5Br + CO\left\{\begin{array}{l} Cl \\ OC_2H_5 \end{array}\right. + Na_2 = C_6H_5.CO.OC_2H_5 + NaBr + NaCl$$

(4.) When the sodium salts of formic acid and benzenesulphonic acid are fused together, sodium benzoate is formed:—

$$C_6H_5.SO_3Na + CHO_2Na = HNaSO_3 + C_6H_5.CO_2Na$$

Benzoic acid is also produced, together with phthalic acid $C_6H_4(CO_2H)_2$, formic acid, and other products, by treating benzene with manganese dioxide and dilute sulphuric acid. If some formic acid be previously added to the benzene, the yield of benzoic acid is increased; and from this it appears that benzoic acid is produced by the simultaneous oxidation of benzene and formic acid:—

$$C_6H_6 + CH_2O_2 + O = C_6H_5.CO_2H + H_2O$$

Benzoic acid is obtained from gum benzoin by carefully heating the coarsely-powdered resin in a shallow iron pan, over which a sheet of paper pierced with a number of pin-holes is stretched, and the whole is then covered with a cap of stiff paper. The vapour of the acid condenses in the cap in light, feathery crystals, possessing the fragrant odour of the gum, which is due to a small quantity of a volatile oil. A more productive method consists in boiling the resin with milk of lime, concentrating the filtrate, and precipitating the acid by hydrochloric acid.

Benzoic acid, being used in the manufacture of aniline colours, is now prepared in quantity from naphthalene $C_{10}H_8$, a hydrocarbon occurring in the heavy coal-tar oil. It is first oxidized to phthalic acid $C_6H_4(CO_2H)_2$, and the calcium salt of this acid is mixed with slaked lime, and heated for several hours to 300°—350°:—

$$2C_6H_4(CO_2)_2Ca + Ca(OH)_2 = (C_6H_5.CO_2)_2Ca + 2CaCo_3$$

Phthalic acid may also be converted into benzoic acid by distilling its ammonium salt, which is thus converted into *phthalimide* $C_6H_4(CO_2)NH$. On distilling this body with lime, it yields benzonitrile:—

$$C_6H_4(CO)_2NH + CaO = C_6H_5.CN + CaCO_3$$

The nitrile is boiled with caustic soda, and the sodium salt decomposed by hydrochloric acid.

Benzoic acid is also obtained from urine of cows and horses, as will be described under Hippuric Acid.

Benzoic acid crystallizes from a hot aqueous solution in large, thin, flexible, and brilliant needles or plates, melting at 120°. It boils at 250°, but sublimes readily at a much lower temperature, and volatilizes by boiling its solution. It is only sparingly soluble in cold water, but readily in boiling water and in alcohol. It has a peculiar aromatic odour, which, on heating the acid, becomes irritating, and produces coughing.

It is very characteristic of this acid that the presence of mere traces of certain impurities prevents the crystallization and lowers the melting-point. Thus, on oxidizing toluene with dilute nitric acid, a benzoic acid is obtained containing nitrobenzoic acid. By distilling it with steam, the latter acid is almost entirely left behind; only a trace, so small that it cannot be detected by combustion-analysis, is carried over; yet the benzoic acid can, even by repeated recrystallization, only be obtained in warty crusts or flakes. But on heating it with tin and hydrochloric acid, the nitro-acid is converted into amidobenzoic acid, which on cooling remains in solution, whilst pure benzoic acid crystallizes in the characteristic needles. Before these facts were known, it was believed that several isomeric benzoic acids existed.

Most benzoates are soluble in water; the neutral solutions give with ferric chloride a reddish precipitate of ferric benzoate. This reaction is made use of for the separation of iron from manganese, and for the detection of benzoic acid.

Silver benzoate is very sparingly soluble in cold water, and crystallizes from a boiling solution in small shining plates.

Methyl Benzoate $C_6H_5.CO_2.CH_3$ is readily formed by passing hydrochloric acid gas into a solution of benzoic acid in methyl alcohol. It is a limpid liquid, possessing a fragrant odour, and boiling at 199°. Alkalis decompose it into benzoic acid and methyl alcohol. As this compound has such a high boiling-point, it can easily be obtained pure by using impure methyl alcohol; and it is therefore used for preparing pure methyl alcohol, as the benzoic acid can easily be recovered and employed again for the same purpose.

Ethyl Benzoate $C_6H_5.CO_2.C_2H_5$ is produced by the action of hydrochloric acid on an alcoholic solution of the acid, and by adding benzoyl chloride to ethyl alcohol. It is an aromatic liquid, boiling at 213°.

Benzoyl Chloride $C_6H_5.COCl$ is prepared by distilling the acid with phosphorus trichloride, and also formed by the action of chlorine on benzaldehyde. It is a limpid liquid, boiling at 199°, and possessing a very pungent smell. Water acts on it as on other acid chlorides; and on heating it with phosphorus pentachloride it is converted into *benzenyl trichloride* $C_6H_5.CCl_3$.

Benzoyl Fluoride $C_6H_5.COF$.—To obtain this compound, benzoyl chloride and dry potassium hydrofluoride are heated in a platinum retort:—

$$HKF_2 + 2C_6H_5.COCl = HCl + KCl + 2C_6H_5.COF$$

It is an oily liquid, boiling at 162°, and possessing a very irritating smell. Water decomposes it readily into hydrofluoric acid and benzoic acid.

Benzoyl Oxide or *Benzoic Anhydride* $(C_6H_5.CO)_2O$ is prepared by heating dry sodium benzoate with benzoyl chloride, or with phosphorus oxychloride:—

$$2C_6H_5.CO.ONa + POCl_3 = 2C_6H_5.COCl + NaCl + NaPO_3$$

$$C_6H_5.CO.ONa + C_6H_5.COCl = \left.\begin{matrix}C_6H_5.CO\\C_6H_5.CO\end{matrix}\right\}O + NaCl$$

The mass is exhausted with water, and the residue crystallized from alcohol. Benzoyl oxide forms rhombic prisms, melting at 42°, and boiling at 310°. By boiling water, it is slowly resolved into two molecules of benzoic acid.

Benzoyl-acetyl Oxide $\left.\begin{matrix}C_6H_5.CO\\CH_3.CO\end{matrix}\right\}O$ is produced by acting with acetyl chloride on sodium benzoate, or with benzoyl chloride on fused sodium acetate. It is a colourless, oily liquid, which by distillation is resolved into acetyl oxide and benzoyl oxide:—

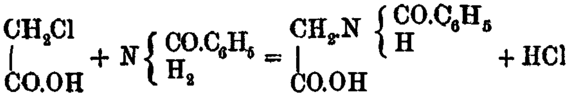
$$\left.\begin{matrix}C_6H_5.CO\\CH_3.CO\end{matrix}\right\}O + \left.\begin{matrix}CH_3.CO\\C_6H_5.CO\end{matrix}\right\}O = \left.\begin{matrix}CH_3.CO\\CH_3.CO\end{matrix}\right\}O + \left.\begin{matrix}C_6H_5.CO\\C_6H_5.CO\end{matrix}\right\}O$$

Benzoyl Dioxide $\left.\begin{matrix}C_6H_5.CO.O\\C_6H_5.CO.O\end{matrix}\right\}$.—To prepare this compound, benzoyl chloride is mixed with *pure* barium dioxide, and the resulting mass exhausted with carbon disulphide or ether. It forms colourless crystals, does not dissolve in water, and is decomposed by heat with a slight detonation. Hot potash-solution resolves it into benzoic acid and oxygen.

Benzamide $C_6H_5.CO.NH_2$ is produced by acting with ammonia on benzoyl chloride or ethyl benzoate. It is sparingly soluble in cold water, and crystallizes from a hot solution in needles, melting at 115°, and boiling at 288°. On heating it with phosphorus pentoxide, it is resolved into water and benzonitrile.

Hippuric or *Benzamidacetic Acid* $C_9H_9NO_3$ occurs as potassium or sodium salt in the urine of all herbivorous animals, and also in small quantity in human urine. When toluene, benzoic acid, oil of bitter almonds, or cinnamic acid, are taken internally, they are converted into hippuric acid, which is found in the urine. This transformation takes place in the human organism, as well as that of many animals. Quinic acid is also converted into hippuric acid, but only in the human system and that of graminivorous animals.

Hippuric acid is also produced by the action of benzoyl chloride on the silver or zinc salts of amidacetic acid, and by heating benzamide with chloracetic acid:—



$$\begin{matrix}CH_2Cl\\|\\CO.OH\end{matrix} + N\left\{\begin{matrix}CO.C_6H_5\\H_2\end{matrix}\right. = \begin{matrix}CH_2.N\left\{\begin{matrix}CO.C_6H_5\\H\end{matrix}\right.\\|\\CO.OH\end{matrix} + HCl$$

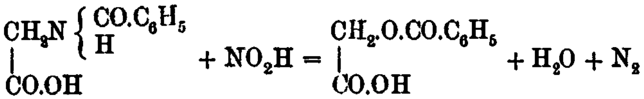
It is generally prepared by evaporating the fresh urine of cows or horses to about one-tenth of its volume, and precipitating with hydrochloric acid.

It forms large rhombic prisms, dissolving sparingly in cold water, but freely in hot water and alcohol. On heating, it fuses, and then decomposes, yielding prussic acid, benzoic acid, benzamide, benzonitrile, &c. By boiling it with alkalis or acids, it is resolved into benzoic acid and amidacetic acid. A similar change takes place when urine undergoes putrefaction, and benzoic acid may therefore be obtained in quantity from the urine of horses or cows.

Hippuric acid is monobasic, and yields a series of salts, which are mostly soluble in water.

By the action of potassium chlorate and hydrochloric acid, it is converted into *monochloro-* and *dichlorohippuric acid.* Monochlorohippuric acid is found in the urine after monochlorobenzoic acid has been taken internally.

Benzoglycollic Acid $C_9H_8O_4$ is obtained by acting with nitrous acid on hippuric acid :—



$$\begin{array}{l} CH_2N\left\{\begin{array}{l}CO.C_6H_5\\ H\end{array}\right. \\ | \\ CO.OH \end{array} + NO_2H = \begin{array}{l} CH_2.O.CO.C_6H_5 \\ | \\ CO.OH \end{array} + H_2O + N_2$$

It crystallizes in colourless prisms, and does not freely dissolve in water.

Benzoleic Acid $C_6H_9.CO_2H$.—This additive compound is formed, together with benzyl alcohol, by acting with sodium amalgam on an aqueous solution of benzoic acid. It is an oily liquid, smelling like valerianic acid, and forms amorphous and deliquescent salts, which, as well as the free acid, absorb oxygen from the air and are converted into benzoates.

SUBSTITUTED BENZOIC ACIDS.

1·3 *Chlorobenzoic Acid* $C_6H_4Cl.CO_2H$ is obtained by acting on benzoic acid with hydrochloric acid and potassium chlorate, and by oxidizing orthochlorotoluene. It is but sparingly soluble in water, and crystallizes in needles, melting at 152°.

1·4 *Chlorobenzoic Acid,* or *Chlorodracylic Acid.*—This acid is formed by oxidizing parachlorotoluene or parachlorobenzyl alcohol with a dilute solution of chromic acid. It sublimes in scaly crystals, melting at 236°.

1·2 *Chlorobenzoic Acid,* or *Chlorosalylic Acid.*—To prepare this acid, 1·2 oxybenzoic or salicylic acid $C_6H_4(OH)CO_2H$ is treated with phosphorus pentachloride, and the *chlorosalyl chloride* $C_6H_4Cl.COCl$ thus formed is decomposed with water. Chlorosalylic acid is much more freely soluble in water than its isomerides, and crystallizes in needles, melting at 137° when in the dry state, but under water already at 100°.

Nascent hydrogen converts the three chlorobenzoic acids into benzoic acid.

α Dichlorobenzoic, or *Dichlorodracylic Acid* $C_6H_2Cl_2.CO_2H$, has been obtained by several reactions. It is formed by oxidizing dichlorotoluene with chromic acid, and by heating *dichlorobenzenyl trichloride* $C_6H_2Cl_2.CCl_3$ (see page 346) with water to 100°. The same acid is produced by heating chlorodracylic acid with antimony pentachloride, and by boiling benzoic acid with a clear solution of bleaching-powder, precipitating with hydrochloric acid, and boiling the precipitate again with bleaching-powder:—

$$(1)\ \begin{matrix} C_6H_5.CO_2H \\ C_6H_5.CO_2H \end{matrix} + Ca\left\{\begin{matrix} OCl \\ OCl \end{matrix}\right. = \left.\begin{matrix} C_6H_4Cl.CO_2 \\ C_6H_4Cl.CO_2 \end{matrix}\right\} Ca + 2H_2O$$

$$(2)\ \begin{matrix} C_6H_4Cl.CO_2H \\ C_6H_4Cl.CO_2H \end{matrix} + Ca\left\{\begin{matrix} OCl \\ OCl \end{matrix}\right. = \left.\begin{matrix} C_6H_3Cl_2.CO_2 \\ C_6H_3Cl_2.CO_2 \end{matrix}\right\} Ca + 2H_2O$$

It crystallizes in slender needles, melting at 202°.

β Dichlorobenzoic, or *Dichlorosalylic Acid*, has been obtained by heating chlorosalylic acid with antimony pentachloride. It crystallizes in glistening needles, melting at 148°.

1·3 *Bromobenzoic Acid* $C_6H_4Br.CO_2H$ is obtained when benzoic acid is heated with bromine and water to 100°. It crystallizes in needles, melting at 154°.

1·4 *Bromobenzoic Acid* is produced by oxidizing parabromotoluene, and forms needles, melting at 251°.

1·2 *Bromobenzoic Acid* has been obtained from the corresponding amidobenzoic acid by converting it into a diazo-compound, and decomposing this by hydrobromic acid. It sublimes in flat needles, melting at 138°.

We know, also, the three *iodobenzoic acids* which have been produced from the corresponding diazo-compounds.

Fluobenzoic Acid $C_6H_4F.CO_2H$ is produced by acting with fuming hydrofluoric acid on diazo-amidobenzoic acid. It crystallizes from an aqueous solution in large rhombic prisms, melting at 182°. It volatilizes with the vapour of water, and forms crystalline salts.

1·3 *Orthonitrobenzoic Acid* $C_6H_4(NO_2)CO_2H$.—To prepare this acid an intimate mixture of one part of benzoic acid and two parts of nitre is added to three parts of sulphuric acid, and then gently heated until the nitro-acid swims as an oily layer on the top. To remove some metanitrobenzoic acid, which forms at the same time, the product is three times exhausted with about twice its quantity of boiling water, and the residue either crystallized from more boiling water, or sublimed. The pure acid forms colourless needles, melting at 140°. It is also obtained by oxidizing orthonitrotoluene.

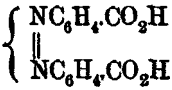
1·2 *Metanitrobenzoic Acid* is formed, but only in small quantity, together with the ortho-acid. The acid, as well as its salts, are much more soluble than their isomerides, and distinguished by their intensely sweet taste, while most other nitro-compounds have a bitter taste. The acid crystallizes by the slow evaporation of an alcoholic solution in large yellowish prisms, melting at 145°.

1·4 *Paranitrobenzoic Acid* is prepared by oxidizing paranitrotoluene, and forms yellowish plates, melting at 240°.

Dinitrobenzoic Acid is formed when 1·3 nitrobenzoic acid is heated with a mixture of nitric and sulphuric acids; it crystallizes in small brilliant plates, and melts at 202°. An isomeride has been obtained oxidizing dinitrotoluene with nitric acid; it forms long prisms, melting at 179°.

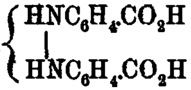
Azobenzoic Acids.—These bodies are formed by acting with sodium-amalgam and water on the nitrobenzoic acids. They are amorphous yellow solids, which are almost insoluble in water, alcohol, ether, &c., and form sparingly soluble salts. Reducing agents convert them into colourless *hydrazobenzoic acids.* The constitution of these bodies corresponds to that of azobenzene, &c.:—

Azobenzoic Acid . .



$$\left\{\begin{array}{l} NC_6H_4.CO_2H \\ \| \\ NC_6H_4.CO_2H \end{array}\right.$$

Hydrazobenzoic Acid



$$\left\{\begin{array}{l} HNC_6H_4.CO_2H \\ | \\ HNC_6H_4.CO_2H \end{array}\right.$$

1·3 *Amidobenzoic Acid* $C_6H_4(NH_2)CO_2H$ is easily obtained by reducing the corresponding nitrobenzoic acid with ammonium sulphide, or with tin and hydrochloric acid. It crystallizes in small prisms, melting at 165°, and dissolving freely in hot, but only sparingly in cold water. It forms metallic salts, and combines as amido-compound also with acids.

1·4 *Amidobenzoic* or *Amidodracylic Acid* crystallizes from water in long slender needles, melting at 187°.

1·2 *Amidobenzoic*, *Amidodracylic*, or *Anthranilic Acid* was first obtained by boiling finely-powdered indigo with caustic soda and manganese dioxide for several days. After the solution has been neutralized with sulphuric acid, it is evaporated, and the residue exhausted with alcohol, which dissolves sodium anthranilate. It is also produced by the reduction of the corresponding nitro-acid, and has further been obtained from 1·3 bromobenzoic acid, which yields two isomeric nitro-compounds; one of these, melting at 141°, is reduced to amidobromobenzoic acid, and the latter treated with water and sodium amalgam.

Anthranilic acid is sparingly soluble in cold, and more freely in hot water; it forms thin prisms, melting at 144°; and when more strongly heated, it is resolved into aniline and carbon dioxide. Its isomerides yield also aniline on heating them with an alkali.

Diazobenzoic Acid $C_6H_4\left\{\begin{array}{l}N_2OH \\ CO_2H\end{array}\right.$.—When 1·3 amidobenzoic acid is dissolved in cold nitric acid, and nitrogen trioxide passed into this solution, the *nitrate* of *diazobenzoic acid* $C_6H_4\left\{\begin{array}{l}N_2.NO_3 \\ CO_2H\end{array}\right.$ crystallizes out in colourless prisms. It explodes violently when heated, and is decomposed by boiling water, 1·3 oxybenzoic acid being formed :—

$$C_6H_4\left\{\begin{matrix}N_2.NO_3\\CO_2H\end{matrix}\right. + H_2O = C_6H_4\left\{\begin{matrix}OH\\CO_2H\end{matrix}\right. + HNO_3 + N_2$$

The free acid is obtained by adding an alkali to a solution of the nitrate; it is a yellow body, which soon undergoes spontaneous decomposition

Diazo-amidobenzoic Acid $C_6H_4\left\{\begin{matrix}N_2(NH)C_6H_4.CO_2H\\CO_2H\end{matrix}\right.$ is precipitated in orange crystals by adding amidobenzoic acid to an aqueous solution of diazobenzoic acid. It is almost insoluble in water, and a bibasic acid. When heated, it is decomposed with a slight explosion.

Uramidobenzoic Acid $C_6H_4\left\{\begin{matrix}NH.CO.NH_2\\CO_2H\end{matrix}\right.$.—This compound is distinguished by the great number of derivatives which it yields. It is produced by fusing urea with 1·3 amidobenzoic acid. By the action of strong nitric acid it yields three isomeric dinitro-acids, which, owing to the great similarity of their properties, cannot be separated from each other.

When an ammoniacal solution of these acids is boiled, they are converted into the mononitro-acids :—

$$C_6H_2(NO_2)_2\left\{\begin{matrix}NH.CO.NH_2\\CO_2H\end{matrix}\right. + H_2O$$
$$= C_6H_3(NO_2)\left\{\begin{matrix}NH.CO.NH_2\\CO_2H\end{matrix}\right. + NO_2.OH$$

The mononitro-compounds can easily be separated, their barium salts possessing a very different solubility in water. On acting with nitric acid on the pure mononitro-acids, the dinitro-acids are obtained perfectly pure. They form yellowish-white needles, and are freely soluble in alcohol, but scarcely soluble in water. By boiling them with water for a long time, they are converted into *amido-nitrobenzoic acids* :—

$$C_6H_2(NO_2)_2\left\{\begin{matrix}NH.CO.NH_2\\CO_2H\end{matrix}\right. = C_6H_3(NO_2)\left\{\begin{matrix}NH_2\\CO_2H\end{matrix}\right. + CO_2 + N_2O$$

When these amido-nitro-acids are gently heated with tin and hydrochloric acid, they are reduced to diamidobenzoic acids.

a Diamidobenzoic Acid $C_6H_3\left\{\begin{matrix}(NH_2)_2\\CO_2H\end{matrix}\right.$ is sparingly soluble in hot water, and forms minute prisms. Its sulphate $C_6H_3(CO_2H)(NH_2)_2SO_4H_2$ is almost insoluble in water. On distilling the acid, it is resolved in carbon dioxide and *orthodiamidobenzene* (see page 327).

β Diamidobenzoic Acid is more freely soluble, and crystallizes in pale-yellow plates. The sulphate has the composition $2[C_6H_3(CO_2H)(NH_2)_2]SO_4H_2$, and is more soluble than the *a* compound.

γ *Diamidobenzoic Acid* crystallizes in long yellowish-white needles, and forms an almost insoluble sulphate $2[C_6H_3(CO_2H)(NH_2)_2]SO_4H_2 + 1\frac{1}{2}H_2O$.

The β and γ acids yield, when heated, *metadiamidobenzene* (page 327).

δ *Diamidobenzoic Acid.*—This body has been obtained by reducing dinitrobenzoic acid. It differs from its isomerides by its physical properties, as well as by not yielding a diamidobenzene, being by heat completely carbonized, with the evolution of ammonia.

Sulphobenzoic Acid $C_6H_4\left\{\begin{matrix}SO_3H\\CO_2H\end{matrix}\right.$.—This strong bibasic acid is formed by passing gaseous sulphur trioxide over benzoic acid. It is a crystalline, very deliquescent, sour mass. The neutral barium salt is freely soluble in water, but the acid salt $(C_6H_4SO_3)_2Ba(CO_2H)_2$, which crystallizes in monoclinic prisms, dissolves but sparingly.

Disulphobenzoic Acid $C_6H_3\left\{\begin{matrix}(SO_3H)_2\\CO_2H\end{matrix}\right.$ is obtained by heating benzoic acid with fuming sulphuric acid and phosphorus pentoxide to 250°. It forms hygroscopic crystals. The acid barium salt $C_6H_3\left\{\begin{matrix}(SO_3)_2Ba\\CO_2H\end{matrix}\right. + 2H_2O$, is sparingly soluble in water, and forms microscopic needles; the normal salt $2[C_6H_3(SO_3)_2CO_2]Ba_3 + 7H_2O$, crystallizes in prisms. The lead-salt is insoluble in water.

OXYBENZYL- AND OXYBENZOYL-COMPOUNDS.

The compounds belonging to this group contain one or more hydroxyls, combined with the aromatic nucleus, and have therefore the character of phenols.

Saligenin, or 1·2 *Oxybenzyl Alcohol* $C_6H_4\left\{\begin{matrix}OH\\CH_2.OH\end{matrix}\right.$.—The bark of different kinds of willow contains *Salicin* $C_6H_4\left\{\begin{matrix}OH\\CH_2.OC_6H_{11}O_5\end{matrix}\right.$, a glucoside which, by the actions of certain ferments, takes up water, and is resolved into saligenin and grape-sugar.

Saligenin crystallizes from alcohol or hot water in brilliant, small, rhombic plates, melting at 82°, and subliming above 100°. Its aqueous solution gives with ferric chloride a deep-blue colour. Oxidizing agents convert it into salicyl aldehyde and salicylic acid. Saligenin is isomeric with orcin and homopyrocatechin, and metameric with guaicacol:—

$$\text{Saligenin } C_6H_4\left\{\begin{matrix}OH\\CH_2.OH\end{matrix}\right. \qquad \left.\begin{matrix}\text{Orcin}\\\text{Homo-pyrocatechin}\end{matrix}\right\} C_6H_3\left\{\begin{matrix}(OH)_2\\CH_3\end{matrix}\right.$$

$$\text{Guaicacol } C_6H_4\left\{\begin{matrix}OH\\OCH_3\end{matrix}\right.$$

Saliretin $\left.\begin{matrix}C_6H_4(OH)CH_2\\ C_6H_4(OH)CH_2\end{matrix}\right\}O$ is formed by heating saligenin or salicin with hydrochloric acid. It is a yellowish amorphous powder.

Salicylaldehyde $C_6H_4\left\{\begin{matrix}OH\\ COH\end{matrix}\right.$ exists in the flowers of the meadow-sweet and other species of *Spiræa*, and in the larvæ of *Chrysomela populi*. It is conveniently prepared by distilling salicin with dilute sulphuric acid and potassium dichromate. It is a mobile, colourless liquid, possessing a fragrant smell, and boiling at 196°. At −20° it solidifies, and when exposed to the air it assumes a red tint; it is sparingly soluble in water. Ferric chloride colours this solution deep-violet.

Salicylaldĕhyde forms crystalline compounds with the acid sulphites of the alkali-metals, and as phenol it forms also metallic compounds. The potassium-compound $C_6H_4\left\{\begin{matrix}OK\\ COH\end{matrix}\right.$ crystallizes from water in colourless plates, which, when moist, rapidly absorb oxygen from the air. By adding a solution of copper acetate to an alcoholic solution of the aldehyde, the compound $(C_6H_4)COH)O)_2Cu$ separates out in shining green crystals.

When equal molecules of the aldehyde and phosphorus pentachloride are mixed, *oxybenzylene dichloride* $C_6H_4(OH)CHCl_2$ is formed, crystallizing from ether in large hard prisms, melting at 82°. By distilling this compound with phosphorus pentachloride, it is converted into *chlorobenzylene dichloride* $C_6H_4Cl.CHCl_2$, a colourless and very refractive liquid, boiling at 229°, and possessing a peculiar odour and pungent taste. On heating it with water to 170°, it yields 1·2 *chlorobenzaldehyde* $C_6H_4Cl.COH$, a liquid boiling at 210°, and possessing a pungent taste and smell.

Methyl-Salicylaldehyde $C_6H_4\left\{\begin{matrix}OCH_3\\ COH\end{matrix}\right.$ is formed by acting with methyl iodide on the potassium compound of the aldehyde. It is a liquid possessing a fragraut smell, and boiling at 238°.

Salicylic Acid, or 1·2 *Oxybenzoic Acid*, occurs in the flowers of several species of *Spiræa*, and its methyl-ether forms the chief constituent of oil of wintergreen. It has been produced artificially by passing carbon dioxide into a mixture of sodium and phenol:—

$$C_6H_5.ONa + CO_2 = C_6H_4\left\{\begin{matrix}OH\\ CO_2Na\end{matrix}\right.$$

It is also formed by fusing metacresol with an excess of caustic potash:—

$$C_6H_4\left\{\begin{matrix}OH\\ CH_3\end{matrix}\right. + 2KOH = C_6H_4\left\{\begin{matrix}OK\\ CO_2K\end{matrix}\right. + 3H_2$$

By acting with nitrous acid on a dilute solution of anthranilic acid (page 365), salicylic acid is obtained:—

$$C_6H_4\left\{\begin{matrix}NH_2\\CO_2H\end{matrix}\right. + NO_2H = C_6H_4\left\{\begin{matrix}OH\\CO_2H\end{matrix}\right. + N_2 + H_2O$$

To prepare salicylic acid, wintergreen-oil is boiled with caustic potash; methyl alcohol distils over, and potassium salicylate is left behind.

Salicylic acid crystallizes in four-sided prisms, melting at 156°; it is sparingly soluble in water. The aqueous solution gives, with ferric chloride, a deep-violet colour. When a small quantity of the acid is carefully heated, it sublimes; but on heating it quickly, or in presence of alkalis, it splits up into phenol and carbon dioxide.

It is a monobasic acid, but as phenol it forms also compounds containing two equivalents of a metal; but these are very unstable, and decomposed by carbon dioxide.

Methyl Salicylate $C_6H_4\left\{\begin{matrix}OH\\CO.OCH_3\end{matrix}\right.$ is the chief constituent of oil of wintergreen, and forms a colourless liquid, possessing a fragrant odour, and boiling at 224°. It forms, with alkalis, unstable phenates.

Methyl-salicylic Acid $C_6H_4\left\{\begin{matrix}OCH_3\\CO_2H\end{matrix}\right.$.—The methyl-ether of this acid is produced by heating oil of wintergreen with caustic potash and methyl iodide. By boiling this ether with an alkali, it is decomposed into methyl alcohol and methyl-salicylic acid, which crystallizes in plates, melting at 98°·5. On heating it to 200°, it is resolved into carbon dioxide and anisol (see page 332). This acid is isomeric with methyl salicylate, from which it differs by being a strong acid.

Salicylic Anhydride $C_6H_4\left\{\begin{matrix}O\\CO\end{matrix}\right\rangle$ is obtained by acting with phosphorus oxychloride on sodium salicylate:—

$$3C_6H_4\left\{\begin{matrix}OH\\CO.ONa\end{matrix}\right. + POCl_3 = 3C_6H_4\left\{\begin{matrix}O\\CO\end{matrix}\right\rangle + NaPO_4 + 3HCl$$

It is a white powder, which is insoluble in water, and forms, with potash, potassium salicylate.

Salicylamide $C_6H_4\left\{\begin{matrix}OH\\CO.NH_2\end{matrix}\right.$ is produced by the action of ammonia on oil of wintergreen. It forms small plates, melting at 132°, and subliming when more strongly heated. With caustic potash it forms the compound $C_6H_4\left\{\begin{matrix}OK\\CO.NH_2\end{matrix}\right.$; by adding silver nitrate to an aqueous solution of this phenate, the silver-compound $C_6H_4\left\{\begin{matrix}OAg\\CO.NH_2\end{matrix}\right.$ is precipitated in white flakes.

At 270°, the amide is resolved into water and *salicylnitrile* $C_6H_4\left\{\begin{matrix}OH\\CN\end{matrix}\right.$, a crystalline solid, which is insoluble in water, and dissolves in ammonia. The salts of heavy metals precipitate from this solution the corresponding phenates.

Phosphorus pentachloride converts salicylic acid into chlorosalyl chloride (page 363), and by the action of chlorine or bromine it yields products of substitution. When it is treated with iodine and iodic acid, one or more hydrogen-atoms are replaced by iodine.

All these substituted salicylic acids are resolved at a high temperature into carbon dioxide and substituted phenols.

Nitrosalicylic Acid $C_6H_3(NO_2)\left\{\begin{matrix}OH\\CO_2H\end{matrix}\right.$ is formed by dissolving salicylic acid or salicin in fuming nitric acid, and by boiling indigo with dilute nitric acid. It crystallizes in thin needles, and forms two series of salts; those containing two equivalents of a metal possess a yellow colour.

Amidosalicylic Acid $C_6H_3(NH_2)\left\{\begin{matrix}OH\\CO_2H\end{matrix}\right.$ is produced by reducing nitrosalicylic acid. It forms shining needles, and combines with bases as well as with acids. By the action of heat it is decomposed into carbon dioxide and ortho-amidophenol.

1·3 *Oxybenzoic Acid.*—This isomeride of salicylic acid is commonly called simply oxybenzoic acid. It is produced by passing nitric trioxide into a boiling solution of 1·3 amidobenzoic acid, or by boiling the nitrate of the corresponding diazobenzoic acid with water. It has also been obtained by fusing sulphobenzoic acid, 1·3 chlorobenzoic acid, or orthocresol with caustic potash.

It crystallizes in prismatic needles, is readily soluble in boiling water, and possesses a sweet taste. It melts at 195°, and at a very high temperature is resolved into phenol and carbon dioxide. The same decomposition occurs much more readily in presence of an alkali. With ferric salts it gives no reaction.

Methyl-oxybenzoic Acid $C_6H_4\left\{\begin{matrix}OCH_3\\CO.OH\end{matrix}\right.$—The sodium salt of this acid is formed by passing carbon dioxide into a mixture of bromophenol-methylether and sodium:—

$$C_6H_4\left\{\begin{matrix}OCH_3\\Br\end{matrix}\right. + Na_2 + CO_2 = C_6H_4\left\{\begin{matrix}OCH_3\\CO.ONa\end{matrix}\right. + NaBr$$

By decomposing this salt with hydrochloric acid, the free acid is obtained, which crystallizes in long needles, melting at 95°, and subliming without decomposition.

It has also been produced by heating oxybenzoic acid with methyl iodide and caustic potash:—

$$C_6H_4\left\{\begin{matrix}OK\\CO.OK\end{matrix}\right. + 2CH_3I = C_6H_4\left\{\begin{matrix}OCH_3\\CO.OCH_3\end{matrix}\right. + 2KI$$

and decomposing the ether thus produced with potash:—

$$C_6H_4\left\{\begin{matrix}OCH_3\\CO.OCH_3\end{matrix}\right. + KOH = C_6H_4\left\{\begin{matrix}OCH_3\\CO.OK\end{matrix}\right. + CH_3.OH$$

1·4 *Para-oxybenzoic Acid.*—This third isomeric acid is obtained by the action of nitrous acid upon an aqueous solution of paramidobenzoic acid, as well as by the action of fusing caustic potash upon anisic acid, paracresol and many resins (gum benzoin, aloes, dragon's-blood, &c.).

It is much more soluble in water than salicylic acid, and crystallizes in monoclinic prisms, with one molecule of water. It melts at 210°, decomposing at the same time partly into carbon dioxide and phenol. Its aqueous solution gives with ferric chloride a yellow precipitate. Phosphorus pentachloride converts it into parachlorobenzoyl chloride.

Anisyl Aldehyde, or Methyl-para-oxybenzaldehyde $C_6H_4\left\{\begin{array}{l}OCH_3\\COH\end{array}\right.$.—The volatile oils of *Pimpinella Anisa, Anethum Fœniculum, Artemisia Dracunculus,* and other Umbelliferæ, and the oil of *Illicium anisatum,* contain as principal constitutent *anethol* $C_6H_4\left\{\begin{array}{l}OCH_3\\C_3H_5\end{array}\right.$, which, by the action of dilute nitric acid or chromic acid, is oxidized to anisyl aldehyde, an oily liquid, boiling at 248°, and possessing an aromatic odour. It forms with the acid sulphites of the alkali-metals crystalline compounds, and combines with nascent hydrogen with the formation of *Anisyl alcohol* or *methyl-para-oxybenzyl alcohol* $C_6H_4\left\{\begin{array}{l}OCH_3\\CH_2.OH\end{array}\right.$, which crystallizes in shining prisms, melting at 28°, and boiling at about 250°. It has a faint odour and burning taste; on heating it with hydrochloric acid it is converted into the liquid *anisyl chloride* $C_6H_4\left\{\begin{array}{l}OCH_3\\CH_2Cl\end{array}\right.$.

Anisic Acid, or *Methyl-para-oxybenzoic Acid* $C_6H_4\left\{\begin{array}{l}OCH_3\\CO.OH\end{array}\right.$, is formed by the prolonged action of oxidizing agents upon the above-mentioned oils, and on paracresol-methyl-ether, and has also been produced by heating para-oxybenzoic acid with caustic potash and methyl iodide. It crystallizes in colourless needles, melting at 175°, and subliming without undergoing decomposition. By heating it with hydrochloric acid or hydriodic acid, or by fusing it with caustic potash, it yields para-oxybenzoic acid, and by distillation with caustic baryta it is resolved into carbon dioxide and anisol.

Nitranisic Acid $C_6H_3(NO_2)\left\{\begin{array}{l}OCH_3\\CO.OH\end{array}\right.$ is obtained by acting on oil of anise-seed with hot nitric acid of specific gravity of 1·4, and forms small glistening needles, melting at 180°.

Dinitranisic Acid $C_6H_2(NO_2)_2\left\{\begin{array}{l}OCH_3\\CO.OH\end{array}\right.$ is formed together with di- and trinitranisol, when nitranisic acid is boiled with fuming nitric acid. It crystallizes from hot water in large yellowish, shining needles, melting at 173°. In alcoholic potash it dissolves with a fine red colour, and boiling alkalis decompose it with the formation of dinitropara-oxybenzoic acid.

By acting with ammonia on dinitranisic acid, it is converted into methyl alcohol, and *chrysanisic* or *dinitroparamidobenzoic acid* $C_6H_2(NO_2)_2\left\{\begin{matrix}NH_2\\CO_2H\end{matrix}\right.$ crystallizing from alcohol in small rhombic golden-yellow plates, melting at 259°.

Tin and hydrochloric acid reduce it to *triamidobenzoic acid* $C_6H_2(NH_2)_3CO_2H$, which crystallizes from hot water in fine, shining needles. With sulphuric acid, containing a trace of nitric acid, it forms a deep-blue solution, like *triamidobenzene* (see page 327). It combines not only with bases, but also with acids.

Oxysalicylic Acid $C_6H_3\left\{\begin{matrix}(OH)_2\\CO_2H\end{matrix}\right.$.—To obtain this compound, moniodosalicylic acid is boiled down with caustic potash, the residue dissolved in water, and acidulated with sulphuric acid. The solution is then shaken with ether, and the ethereal solution evaporated. Oxysalicylic acid crystallizes from water in shining needles, melting at 183°, and decomposing when more strongly heated into carbon dioxide, and a mixture of hydroquinone and pyrocatechin. By adding ferric chloride to its aqueous solution, a deep-blue colour is produced, which is changed into red by ammonia.

Protocatechuic Acid $C_6H_3\left\{\begin{matrix}(OH)_2\\CO_2H\end{matrix}\right.$ has been obtained by acting with fused potash on sulphoxybenzoic acid; on bromo-, iodo-, and sulpho-para-oxybenzoic acids; and on bromanisic, eugenic, and piperic acids. It is also formed, together with para-oxybenzoic acid, by fusing gum-benzoin, guaiacum, dragon's-blood, and other resins with potash. It is sparingly soluble in cold water, and crystallizes from boiling water in needles containing one molecule of water. It melts at 200°, and is resolved by dry distillation into carbon dioxide, pyrocatechin and hydroquinone. With ferric chloride it gives a bluish-green colour, which alkalis change into red.

As pyrocatechuic acid may be obtained from 1·3 oxybenzoic acid, as well as from 1·4 paraoxybenzoic acid, it follows that the hydroxyls occupy the positions 3·4.

a Dioxybenzoic Acid $C_6H_3\left\{\begin{matrix}(OH)_2\\CO_2H\end{matrix}\right.$ is produced by converting 1·4 nitrotoluene into the corresponding diazotoluene-sulphonic acid. boiling the latter with water, and fusing the cresol-sulphonic acid thus formed with potash. It is readily soluble in water, and crystallizes in needles; its solution colours ferric salts reddish-brown.

When the above-mentioned diazotoluene-sulphonic acid is boiled with absolute alcohol, and the toluenesulphonic acid thus formed is fused with potash, metacresol is obtained, which by oxidation yields salicylic acid. Consequently the two hydroxyls of *a* dioxybenzoic acid have the position 2·4.

β Dioxybenzoic Acid.—This fourth isomeride is obtained by fusing disulphobenzoic acid with potash. It crystallizes from an aqueous solution in thick prisms, and is not coloured by ferric chloride.

Gallic Acid, or Trioxybenzoic Acid $C_6H_2\left\{\begin{matrix}(OH)_3\\CO_2H\end{matrix}\right.$, occurs in the free state, or as glucoside (tannin) in nutgalls, in the leaves of the bearberry, in tea, in the fruits of *Cæsalpinia coriaria* (Divi-Divi), in the root-bark of the pomegranate, and in other plants. It is obtained by boiling tannin with dilute acids, or exposing it in the moist state to the air at a temperature of 20° to 30°.

Gallic acid is also formed by heating di-iodosalicylic acid with potassium carbonate and by fusing bromocatechuic or β bromodioxybenzoic acid with caustic potash.

The formation of gallic acid from salicylic acid and pyrocatechuic acid proves that the hydroxyls have the position 2. 3. 4 (or 3. 4. 6).

Gallic acid dissolves in 100° parts of cold, and three parts of boiling water, and crystallizes in fine silky needles, containing one molecule of water. It has a slightly acid and astringent taste, and gives a deep-blue colour with ferric salts. It melts at 200°, and at 210° it is resolved into carbon dioxide and pyrogallol.

It forms four series of salts, which are stable in the dry state, or if the solution is acid; but in an alkaline solution they rapidly absorb oxygen, and colour brown and black. From a solution of silver or gold it precipitates the metals.

Ethyl Gallate $C_6H_2\left\{\begin{matrix}(OH)_3\\CO_2.C_2H_5\end{matrix}\right.$ is formed by passing hydrochloric acid gas into a solution of the acid in absolute alcohol. It crystallizes from water in rhombic prisms, possessing a bitter taste and acid reaction. On heating it carefully, it sublimes in brilliant needles. It colours ferric salts blue; forms, as phenol, metallic compounds; and reduces the solutions of the noble metals.

Digallic Acid $\left.\begin{matrix}C_6H_2(OH)_3CO\\C_6H_2(CO_2H)(OH)_2\end{matrix}\right\}O$ is formed by heating gallic acid with phosphorus oxychloride, or by boiling its aqueous solution with arsenic acid. Digallic acid is an amorphous yellowish powder, having a strong astringent taste, and giving with ferric salts a dark-blue colour. By boiling it with hydrochloric acid, it is reconverted into gallic acid. Commercial tannin, or tannic acid (see Glucosides), appears to contain digallic acid in considerable quantity.

Ellagic Acid $C_{14}H_6O_8$ is formed, together with gallic acid, by exposing an aqueous solution of tannic acid to the air, and by heating gallic acid with dry arsenic acid, the latter being reduced to arsenic trioxide. Ellagic acid also occurs in certain "Oriental bezoar-stones," or calculi found in the intestines of wild goats in Persia. It is a yellowish crystalline powder, and insoluble in water.

Quinic or *Kinic Acid* $C_6H_7(OH)_4CO_2H$ occurs in the cinchona-barks, in the leaves of bilberry, in coffee, and in other plants, and is obtained as a by-product in the manufacture of quinine. It is readily soluble in water, and crystallizes in rhombic prisms, melting at 162°. By dry distillation it is decomposed, yielding hydroquionne pyrocatechin, phenol, benzoic acid, &c. Manganese dioxide and sulphuric acid oxidize it to quinone.

By heating it with concentrated hydriodic acid, it is reduced to benzoic acid:—

$$C_6H_7(OH)_4CO_2H + 2HI = C_6H_5.CO_2H + 4H_2O + I_2$$

Phosphorus pentachloride converts it into chlorobenzoyl chloride:—

$$C_6H_7(OH)_4CO.OH + 5PCl_5 = C_6H_4Cl.COCl + 5POCl_3 + 8HCl$$

By fusing it with potash, it yields pyrocatechuic acid:—

$$C_6H_7(OH)_4CO_2H + KOH = C_6H_3(OH)_2CO_2K + 3H_2O + H_2$$

These reactions show that quinic acid is an additive product, containing an aromatic nucleus, in which each carbon atom is linked to an other only by one combining unit.

The quinates are soluble in water. *Calcium quinate* $(C_6H_7(OH)_4CO_2)_2Ca + 10H_2O$ occurs in cinchona-barks, and forms large rhombic crystals.

COMPOUNDS WITH EIGHT ATOMS OF CARBON.

(1) Dimethyl-benzene $C_6H_4\left\{\begin{matrix}CH_3\\CH_3\end{matrix}\right.$ existing in three isomeric modifications.

(2) Ethyl-benzene . . $C_6H_5.C_2H_5$

(3) Ethenyl-benzene . $C_6H_5.C_2H_3$

(4) Ethinyl-benzene . $C_6H_5.C_2H$

DIMETHYL-BENZENES $C_6H_4\left\{\begin{matrix}CH_3\\CH_3\end{matrix}\right.$

When purified coal-naphtha is submitted to fractional distillation, a liquid is obtained, boiling constantly at 139° to 140°. This was formerly regarded as a pure compound, and called *xylene* or *xylol*. More recent researches have, however, shown that xylene is a mixture of two dimethyl-benzenes, which, having nearly the same boiling-point, cannot be separated by distillation.

METHYL-TOLUENE, OR 1·4 DIMETHYL-BENZENE,

Occurs sometimes in quantity in coal naphtha. The pure hydrocarbon is obtained by the action of sodium on a mixture of methyl iodide, and crystallized bibromobenzene, or 1·4 bromotoluene.

It is a colourless liquid, boiling at 136°, solidifying at 15° to a crystalline mass, and possessing a peculiar smell, which is quite different from that of benzene. Fuming nitric acid converts it into two dinitro-compounds, which are separated by crystallizing them from alcohol.

α Dinitromethyl-toluene $C_6H_2(NO_2)_2(CH_3)_2$ forms long, thin, colourless needles, melting at 123°·5. *β Dinitromethyl-toluene* is more freely soluble, and forms long, transparent, monoclinic crystals, melting at 93°.

Trinitromethyl-toluene $C_6H(NO_2)_3(CH_3)_2$ is produced by treating the hydrocarbon with a mixture of nitric and sulphuric acids; it crystallizes from alcohol in long colourless needles, melting at 137°.

Monobromomethyl-toluene $C_6H_3Br(CH_3)_2$.—To prepare this compound, bromine is slowly added to the hydrocarbon, which is cooled down to 0°. It is a colourless liquid, boiling at 205°, and possessing an agreeable odour. By the further action of bromine, it is converted into *dibromomethyl-toluene* $C_6H_2Br_2(CH_3)_2$, crystallizing from alcohol in pearly scales, melting at 72°.

ISOXYLENE, OR 1·3 DIMETHYL-BENZENE,

Forms generally the chief portion of coaltar-xylene, and is obtained pure by distilling mesitylenic acid $C_6H_3(CH_3)_2CO_2H$ with lime. It is a limpid liquid, boiling at 138°, and smelling like methyl-toluene. It is only slowly acted upon by nitric acid, whilst methyl-toluene is readily oxidized by it to toluic acid, and therefore an almost pure isoxylene may be prepared by heating coaltar-xylene, which contains much isoxylene, with dilute nitric acid.

The substitution-products of this hydrocarbon have mostly been obtained from crude xylene, and many of them are, therefore, probably mixtures.

Monochloro-isoxylene $C_6H_3Cl(CH_3)_2$ is produced when xylene is acted on by chlorine either in the cold or in presence of iodine; it is a colourless liquid, boiling at 183°.

Monobromo-isoxylene $C_6H_3Br(CH_3)_2$ is a liquid, boiling at 205°, and possessing an aromatic odour.

Dibromo-isoxylene $C_6H_2Br_2(CH_3)_2$ crystallizes in pearly scales, melts at 69°, and boils at 256°.

Nitro-isoxylene $C_6H_3(NO_2)(CH_3)_2$ is formed, together with dinitro-isoxylene, by dissolving the hydrocarbon in cold, fuming nitric acid. It is a pale-yellow liquid, boiling at 239°.

Dinitro-isoxylene $C_6H_2(NO_2)_2(CH_3)_2$ crystallizes from alcohol in long brilliant prisms, melting at 93°.

Trinitro-isoxylene $C_6H(NO_2)_3(CH_3)_2$ forms colourless crystals, melting at 177°.

Amido-isoxylene $C_6H_3(NH_2)(CH_3)_2$ is a colourless liquid, boiling at 216°, and forming crystallizable salts.

ORTHOXYLENE, OR 1·2 DIMETHYL-TOLUENE.

This hydrocarbon has been obtained by distilling paraxylic acid $C_6H_3(CH_3)_2CO_2H$ with lime. It is a liquid, boiling at 140°, and possessing a peculiar, unpleasant odour. It does not form readily solid nitro-compounds.

XYLENOLS.

Isoxylenol $C_6H_3(OH)(CH_3)_2$.—When mesitylenesulphonic acid is heated with potash to 250°, it is converted into oxymesitylenic acid, which, by heating the fused mass to 290°, is changed into isoxylenol:

$$(1)\quad C_6H_2(CH_3)_3SO_3K + 3KOH = C_6H_2(CH_3)_2\left\{\begin{matrix}OK\\ CO_2K\end{matrix}\right. + 3H_2O$$

$$(2)\quad C_6H_2(CH_3)_2\left\{\begin{matrix}OK\\ CO_2K\end{matrix}\right. + KOH = C_6H_3(CH_3)_2OK + K_2CO_3$$

It is a crystalline solid, melting at 75°, and boiling at 216°.

By dissolving crude xylene in sulphuric acid, and fusing the xylenesulphonic acid with caustic potash, two xylenols are obtained; one seems to be identical with that obtained from mesitylene, and the other is a colourless, strongly refractive liquid, boiling at 211°·5.

Phlorone, or *Xyloquinone* $C_6H_2(CH_3)_2O_2$, is produced by treating coaltar-oil or creosote, boiling above 210°, with manganese dioxide and sulphuric acid. It forms golden-yellow, oblique, rhombic prisms; on heating, it gives off a very pungent smell, which attacks violently the eyes and mucous membranes. It is soluble in boiling water, and sublimes on heating.

Hydrophlorone, or *Xylohydroquinone* $C_6H_2(CH_3)_2(OH)_2$, is obtained by reducing phlorone with sulphurous acid, and crystallizes from boiling water in white, pearly scales.

Beta-orcin $C_8H_8(OH)_2$ is obtained from usnic acid, and similar acids occurring in lichens, by the same method by which orcin is prepared from orsellinic acid. It is soluble in water and alcohol, and crystallizes in colourless prisms, which may be sublimed. Its ammoniacal solution colours red in the air, and with caustic alkalis it yields a red colouring matter. Beta-orcin is probably a di-oxyxylene.

TOLYL- AND TOLUYL-COMPOUNDS.

Tolyl or *Xylyl Chloride* $C_6H_4\left\{\begin{matrix}CH_3\\CH_2Cl\end{matrix}\right.$ is produced by passing chlorine into boiling xylene (isoxylene); it is a liquid having a disagreeable smell, and boiling at 193°:

Tolyl Alcohol $C_6H_4\left\{\begin{matrix}CH_3\\CH_2.OH\end{matrix}\right.$.—When the chloride is heated with silver acetate, it yields *tolyl acetate*, a liquid possessing an aromatic odour, and boiling at 226°. Alkalis convert it into tolyl alcohol, a crystalline solid, forming white needles, which melt at 59°, and boil at 217°.

Tolylamine $C_6H_4\left\{\begin{matrix}CH_3\\CH_2.NH_2\end{matrix}\right.$.—The three tolylamines are formed by heating the chloride with alcoholic ammonia. They neutralize acids, and form crystalline salts. The monamine is a limpid and very alkaline liquid, boiling at 196°, and smelling like herring's brine.

Ditolylamine $[C_6H_4(CH_3)(CH_2)]_2NH$ is a similar body, and *tritolylamine* $[C_6H_4(CH_3)(CH_2)]_3N$ is a viscid liquid, having a faint alkaline reaction. The di- and triamine are decomposed by heat.

1·4 *Paratoluic Acid* $C_6H_4\left\{\begin{matrix}CH_3\\CO_2H\end{matrix}\right.$ is produced by boiling methyl-toluene or cymene for several days with nitric acid of 20 per cent., and distilling the product with steam, or treating it with tin and hydrochloric acid. The same acid has been obtained by passing carbon dioxide into a mixture of 1·4 bromotoluene and sodium.

Paratoluic acid forms slender needles, melting at 178°; it is sparingly soluble in cold, readily in hot water, and forms a number of substitution-products resembling those of benzoic acid.

Paratoluonitrile $C_6H_4(CH_3)CN$ has been prepared by acting on crystallized toluidine with carbon disulphide, and distilling the sulphocarbotoluide thus formed with finely-divided copper, the reaction taking place in three stages. First, the toluide is resolved into tolyl mustard-oil and toluidine; then the copper removes the sulphur from the former compound, tolylcarbamine being produced, which at the high temperature is converted into the nitrile:—

$$(1)\quad CS\left\{\begin{matrix}NH.C_6H_4.CH_3\\NH.C_6H_4.CH_3\end{matrix}\right. = NH_2.C_6H_4.CH_3 + CS.N.C_6H_4.CH_3$$

$$(2)\quad CS.N.C_6H_4.CH_3 + 2Cu = CN.C_6H_4.CH_3 + Cu_2S$$

$$(3)\quad CN.C_6H_4.CH_3 = NC.C_6H_4.CH_3$$

Paratoluonitrile forms fine white needles, melting at 30°, and smelling like oil of bitter almonds. By heating it with concentrated hydrochloric acid to 200°, it is converted into paratoluic acid.

1·3 *Isotoluic Acid* is formed by oxidizing isoxylene, but is more conveniently prepared by heating the calcium-salt of uvitic acid $C_6H_3(CH_3)(CO_2H)_2$ with slaked lime above the melting-point of lead; this reaction is quite analogous to the formation of benzoic acid from phthalic acid. Isotoluic acid crystallizes from water in needles, melting at 105°.

1·2 *Orthotoluic Acid* has been obtained by boiling orthoxylene with dilute nitric acid. It crystallizes from a hot, dilute, aqueous solution in long, transparent, pointed prisms, melting at 102°.

Orthotoluonitrile is produced by converting pseudotoluidine into the corresponding mustard-oil, and distilling the latter with finely-divided copper. It is a refractive liquid, smelling like nitrobenzene, and boiling at 204°. By heating it with hydrochloric acid to 200°, it is converted into orthotoluic acid; but alcoholic potash acts only slowly on it, converting it into *orthotoluylamide* $C_6H_4\left\{\begin{array}{l}CH_3\\CO.NH_2\end{array}\right.$, crystallizing from boiling water in very long and slender needles, melting at 138°.

TOLYLENE-COMPOUNDS.

Tolylene Glycol $C_6H_4\left\{\begin{array}{l}CH_2.OH\\CH_2.OH\end{array}\right.$.—The chloride of this alcohol is produced by passing chlorine into boiling methyl-toluene. It is easily converted into the glycol by heating it with thirty parts of water for three hours to 180°. To isolate the glycol, the solution is allowed to evaporate at the ordinary temperature, and not on a water-bath, because when the hydrochloric acid becomes concentrated a part of the alcohol is reconverted into the chloride. The concentrated solution is neutralized and shaken with ether, the ether evaporated, and the residue crystallized from water *in vacuo*. Tolylene glycol forms white, opaque, interlaced needles, melting at 113°. By heating it with chromic acid solution, it is oxidized to terephthalic acid $C_6H_4(CO_2H)_2$.

Tolylene Dichloride $C_6H_4(CH_2Cl)_2$ is also produced by distilling the glycol with hydrochloric acid; it crystallizes from alcohol in hard, large, transparent, clinorhombic laminæ, melting at 100°, and boiling at 240° to 245°. By dissolving it in fuming nitric acid, it is converted into *nitrotolylene dichloride* $C_6H_3(NO_2)(CH_2Cl)_2$, crystallizing from alcohol in small brilliant plates, melting at 35°, and possessing an agreeable smell.

Tolylene Dibromide $C_6H_4(CH_2Br)_2$ is produced by adding bromine drop by drop to boiling methyl-toluene, and by distilling the glycol with hydrobromic acid. It crystallizes from alcohol in small pearly plates, which are isomorphous with the chloride, and from chloroform in hard brilliant crystals, melting at 146°. In the preparation of this body from the hydrocarbon, higher brominated products are formed at the same time, the vapours of which attack the eyes horribly.

Tolylene Di-iodide $C_6H_4(CH_2I)_2$ is obtained by distilling the glycol with hydriodic acid. It crystallizes in small, rhomboïdal plates, which are decomposed by heat.

Tolylene Monobenzoate $C_6H_4\left\{\begin{matrix}CH_2.OH\\CH_2.OC_7H_5O\end{matrix}\right.$—This ether is formed by heating the chloride with an alcoholic solution of sodium benzoate to 100°. It crystallizes from ether in long, fine, light needles.

Tolylene Diacetate $C_6H_4\left\{\begin{matrix}CH_2.OC_2H_3O\\CH_2.OC_2H_3O\end{matrix}\right.$ has been produced by heating the bromide or chloride with sodium acetate and alcohol to 150°. It forms hard crystals, melting at 47°.

Tolylene Monethyl-Ether $C_6H_4\left\{\begin{matrix}CH_2.OH\\CH_2.OC_2H_5\end{matrix}\right.$ is obtained by boiling the chloride with concentrated alcoholic potash, as a fragrant liquid boiling at 252°.

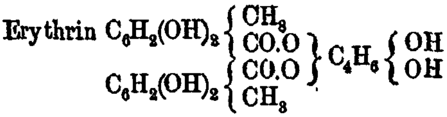
Oxymethyl-phenylformic, or Tolylene-glycollic Acid $C_6H_4\left\}\begin{matrix}CH_2.OH\\CO.OH\end{matrix}\right.$ —To obtain this acid, bromine vapour is passed into paratoluic acid, heated to 170°, and boiling the product with baryta-water. It is more freely soluble in water than paratoluic acid, and crystallizes in flat needles, melting at about 180°.

OXYTOLUYL-COMPOUNDS.

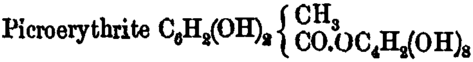
Cresotic Acid $C_6H_3(OH)\left\{\begin{matrix}CH_3\\CO_2H\end{matrix}\right.$ is produced by passing carbon dioxide into a mixture of sodium and coaltar-cresol. It crystallizes from hot water in brilliant needles, melting at 174°, and giving, with ferric chloride, a deep-violet colour.

Orsellinic Acid $C_6H_2(OH)_2\left\{\begin{matrix}CH_3\\CO_2H\end{matrix}\right.$ is produced by boiling erythrin, or lecanoric acid with baryta-water. It is readily soluble in water, crystallizes in prisms, possessing a bitter and sour taste. By dry distillation, or by boiling it for some time with baryta-water or milk of lime, it is resolved into carbon dioxide and orcin $C_6H_3(CH_3)(OH)_2$ (see page 352).

Erythrin $C_{20}H_{22}O_{10}$.—This compound, which is also called erythric acid, occurs in the lichens which are used for preparing archil, the finest kind of which is obtained from *Rocella tinctoria.* It is prepared by boiling this lichen with milk of lime, and precipitating the filtered solution with hydrochloric acid. The precipitate is dried and crystallized from warm alcohol. It is almost insoluble in water, and forms crystalline globular masses. By boiling it with water, it is resolved into *picroerythrite* $C_{12}H_{10}O_7$, a crystalline, bitter substance, and orsellinic acid. If the ebullition be continued, or if erythrin be boiled with baryta-water, *erythrite* $C_4H_6(OH)_4$ (page 277) and *orsellinic acid* are produced. These reactions show that both erythrin and picro-erythrite are orsellinic ethers of the tetrad alcohol erythrite, and have the following constitution:—

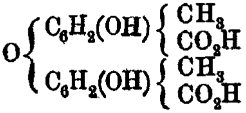


$$\text{Erythrin}\ \begin{matrix} C_6H_2(OH)_2\left\{\begin{matrix}CH_3\\CO.O\end{matrix}\right. \\ C_6H_2(OH)_2\left\{\begin{matrix}CO.O\\CH_3\end{matrix}\right.\end{matrix}\!\!\left.\begin{matrix}\\ \\\end{matrix}\right\} C_4H_6\left\{\begin{matrix}OH\\OH\end{matrix}\right.$$



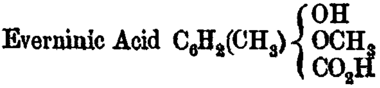
$$\text{Picroerythrite}\ C_6H_2(OH)_2\left\{\begin{matrix}CH_3\\CO.OC_4H_2(OH)_3\end{matrix}\right.$$

Lecanoric Acid, or *Diorsellinic Acid* $C_{16}H_{14}O_7$, is found in a variety of *Rocella tinctoria* growing in South America, and in other lichens, and is prepared in the same way as orsellinic acid. It crystallizes from alcohol in prisms. On boiling it with baryta-water, it yields as first product, only orsellinic acid, and has, therefore, the following constitution:—

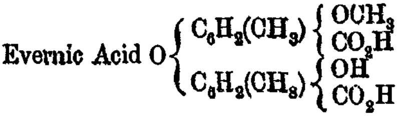


$$O\left\{\begin{matrix}C_6H_2(OH)\left\{\begin{matrix}CH_3\\CO_2H\end{matrix}\right.\\ C_6H_2(OH)\left\{\begin{matrix}CH_3\\CO_2H\end{matrix}\right.\end{matrix}\right.$$

Evernic Acid, or *Methyl-lecanoric Acid* $C_{17}H_{16}O_7$, is found in *Evernia Prunastri*, and is resolved by boiling it with baryta-water into *orsellinic acid* and *everninic acid* $C_9H_{10}O_4$, which crystallizes from hot water in needles. The constitution of these acids is explained by the following formulæ:—

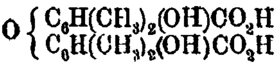


$$\text{Everninic Acid}\ C_6H_2(CH_3)\left\{\begin{matrix}OH\\OCH_3\\CO_2H\end{matrix}\right.$$



$$\text{Evernic Acid}\ O\left\{\begin{matrix}C_6H_2(CH_3)\left\{\begin{matrix}OCH_3\\CO_2H\end{matrix}\right.\\ C_6H_2(CH_3)\left\{\begin{matrix}OH\\CO_2H\end{matrix}\right.\end{matrix}\right.$$

Usnic Acid $C_{18}H_{18}O_7$ has been found in *Usnea barbata* and other lichens; it crystallizes from alcohol in brilliant yellowish-white broad needles, and yields on distillation *beta-orcin* $C_8H_{10}O_2$ (page 376). The constitution of usnic acid is probably similar to that of lecanoric acid, viz.:—



$$O\left\{\begin{matrix}C_6H(CH_3)_2(OH)CO_2H\\C_6H(CH_3)_2(OH)CO_2H\end{matrix}\right.$$

PHTHALIC ACIDS $C_6H_4\left\{\begin{array}{l}CO.OH\\CO.OH\end{array}\right.$

Terephthalic Acid is easily obtained by oxidizing methyl-toluene or any other aromatic hydrocarbon, alcohol, acid, &c., containing two side-chains in the position 1·4, by a solution, consisting of 2 parts of potassium dichromate, 3 parts of sulphuric acid, and 15 parts of water. It is a white crystalline powder, almost insoluble in water, alcohol, and ether, and subliming without previously melting. It forms crystallizable salts; calcium and barium terephthalate are but sparingly soluble in water.

The smallest quantity of terephthalic acid can be easily recognized by treating it with a little phosphorus pentachloride, and adding some methyl alcohol, and then a little water, and shaking the whole with ether. On evaporating the ethereal solution, *methyl terephthalate* separates in crystals, melting at 140°. In the same way *ethyl terephthalate*, melting at 44°, may be obtained.

Hydroterephthalic Acid $C_6H_6(CO_2H)_2$ is a white crystalline powder, which is formed by acting with sodium-amalgam on an alkaline solution of terephthalic acid.

Terephthalonitrile $C_6H_4\left\{\begin{array}{l}CN\\CN\end{array}\right.$ is produced by distilling a mixture of potassium benzene-disulphonate and potassium cyanide. It forms prismatic needles, having an aromatic odour, and dissolving sparingly in alcohol, but not in water. By boiling it with potash, it is converted into terephthalic acid.

Isophthalic Acid is readily formed by boiling isoxylene with chromic-acid solution, and also by oxidizing colophony with nitric acid. It is almost insoluble in cold water, only sparingly in boiling water, but more freely in alcohol, and crystallizes in very thin, long needles, melting above 300°. Isophthalic acid has also been produced by fusing potassium sulphobenzoate with sodium formate:—

$$C_6H_4\left\{\begin{array}{l}SO_3K\\CO_2K\end{array}\right. + CO_2NaH = C_6H_4\left\{\begin{array}{l}CO_2K\\CO_2K\end{array}\right. + SO_3NaH$$

Phthalic Acid is not obtained by oxidizing orthoxylene or orthotoluic acid with chromic acid, because the latter acid burns the phthalic acid completely to carbon dioxide and water, but is formed by oxidizing naphthalene, anthracene, and several derivatives of these hydrocarbons, which contain two carbon-atoms linked to two adjoining carbon-atoms of the aromatic nucleus. It is usually prepared by acting with chlorine on naphthalene, and boiling the product with nitric acid. It crystallizes from boiling water in plates or thick prisms, melting at 175°. Above this temperature it is resolved into water and *phthalic anhydride* $C_6H_4\left\{\begin{array}{l}CO\\CO\end{array}\right\rangle O$, which sublimes in long needles, melting at 129°.

When calcium phthalate is heated with quicklime to 300°, it is converted into calcium benzoate, but at a higher temperature benzene is formed.

Hydrophthalic Acid $C_6H_6\left\{\begin{matrix}CO_2H\\CO_2H\end{matrix}\right.$ is formed by the action of sodium amalgam on an alkaline solution of phthalic acid. It crystallizes in hard monoclinic plates, and yields, on heating, phthalic anhydride.

ETHYL-BENZENE $C_6H_5.C_2H_5$.

This hydrocarbon is produced by acting with sodium on a mixture of bromobenzene, ethyl bromide, and pure ether. It is a limpid, refractive, aromatic liquid, boiling at 134°.

Ethylmonobromobenzene $C_6H_4Br.C_2H_5$ is produced by acting on the hydrocarbon with bromine in the presence of iodine; it is a liquid at 199°.

By adding fuming nitric acid to well-cooled ethyl-benzene until the hydrocarbon is dissolved, two *ethylmonitrobenzenes* $C_6H_4(NO_2)C_2H_5$ are formed. On boiling at 246°, it is oxidized by boiling dilute nitric acid to nitrodracylic acid, whilst the second, boiling at 227°, is completely destroyed by boiling it with nitric acid.

Ethylamidobenzene $C_6H_4(NH_2)C_2H_5$ is obtained from the first of the two nitro-compounds as a limpid liquid, boiling at 214°.

Ethyloxybenzene, or *Ethylphenol* $C_6H_4(OH)C_2H_5$, is formed by dissolving the hydrocarbon in sulphuric acid, and fusing the sulpho-acid with potash. It has great resemblance to common phenol, forming prismatic crystals, melting at 48°, and boiling at 210°.

Phlorol $C_6H_4(OH)C_2H_5$.—This isomeride of ethylphenol has been obtained by distilling phloretic acid $C_6H_4(OH)C_2H_4$ with baryta; it is a liquid boiling at 120°.

STYROLYL-COMPOUNDS.

Styrolyl Chloride $C_6H_5.C_2H_4Cl$ is formed by passing chlorine into boiling ethyl-benzene; it is a liquid boiling with partial decomposition at about 200°.

Styrolyl Bromide $C_6H_5.C_2H_4Br$.—To prepare this compound, pure bromine, which is perfectly free from iodine, is added to cold ethylbenzene. It is a heavy liquid, which may be distilled under a diminished pressure, but under the ordinary atmospheric pressure it is partially resolved into hydrobromic acid and styrolene.

Styrolyl Alcohol $C_6H_5.C_2H_4.OH$.—When the bromide is heated with potassium benzoate, a portion is decomposed into hydrobromic acid and styrolene, whilst another is converted into *styrolyl benzoate*, which forms colourless crystals. This ether is decomposed by alkalis, the alcohol being formed, a heavy liquid, boiling at 225°, and possessing an aromatic odour.

Styrolyl-ethyl Ether $O\left\{\begin{matrix}C_2H_5\\ C_2H_4.C_6H_5\end{matrix}\right.$ is produced by heating the bromide with alcoholic potash or ammonia:—

$$C_6H_5.C_2H_4Br + C_2H_5.OH + NH_3 = \left.\begin{matrix}C_2H_5\\ C_6H_5.C_2H_4\end{matrix}\right\}O + NH_4Br$$

It is a mobile, fragrant liquid, boiling at 187°.

Phenylacetic or Alphatoluic Acid $C_6H_5.CH_2.CO_2H$.—This acid was first obtained by boiling vulpinic acid (see below) with baryta-water. It has been prepared synthetically from its nitrile, and by heating bromobenzene and ethyl chloracetate with silver-dust:—

$$CH_2(Cl)CO_2.C_2H_5 + C_6H_5Br + Ag_2 =$$
$$CH_2(C_6H_5)CO_2.C_2H_5 + AgCl + AgBr$$

Phenylacetic acid forms thin, brilliant plates, melting at 76°·5, and boiling at 261°. Chromic acid oxidizes it to benzoic acid, and when heated with lime it yields toluene. With chlorine, bromine, fuming nitric acid, it gives substitution-products, resembling those of benzoic acid.

Phenylacetonitrile $C_6H_5.CH_2.CN$ is a liquid resembling benzonitrile, and boiling at 229°. It is obtained by distilling benzyl chloride with potassium cyanide.

Vulpinic Acid $C_{19}H_{14}O_5$ exists in *Cetraria vulpina, Parmelia parietina*, and other lichens, and may be extracted from them by chloroform. It crystallizes in lemon-yellow thick prisms, melting at 110°. Boiling baryta-water resolves it into methyl alcohol, oxalic acid, and phenylacetic acid:—

$$C_{19}H_{14}O_5 + 4H_2O = CH_4O + C_2H_2O_4 + 2C_8H_8O_2$$

When it is boiled with dilute potash, it yields methyl alcohol, carbon dioxide, and oxatoluic acid:—

$$C_{19}H_{14}O_5 + 3H_2O = CH_4O + 2CO_2 + C_{16}H_{16}O_3$$

Oxatoluic Acid forms four-sided prisms, melting at 154°, and is monobasic like vulpinic acid. Concentrated boiling potash resolves it into oxalic acid and toluene:—

$$C_{16}H_{16}O_3 + H_2O = C_2H_2O_4 + 2C_7H_8$$

Methyl-phenyl Ketone, or *Acetyl-benzene* $C_6H_5.CO.CH_3$, is obtained by distilling a mixture of calcium benzoate and acetate.

It is a limpid liquid, boiling at 198°. By dissolving it in cold concentrated nitric acid, it is converted into *methyl-mononitrophenyl ketone* $C_6H_4(NO_2)CO.CH_3$, which crystallizes in needles. An isomeride is obtained by the action of hot nitric acid on the ketone as an orange-red, syrupy liquid.

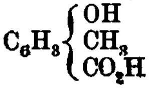
Secondary Styrolyl Alcohol, or *Phenyl-methyl Carbinol* $\left.\begin{matrix} CH_3 \\ C_6H_5 \end{matrix}\right\} CH.OH$ is produced by the action of sodium-amalgam on an alcoholic solution of the ketone. It crystallizes in long prisms, melting at 120°.

Phenylglycolyl Chloride $C_6H_5.CO.CH_2Cl$ is formed by passing chlorine into the boiling ketone; it crystallizes in plates, melting at 41°, boiling at 246°, and possessing a pungent smell.

Phenylglycolyl Acetate $C_6H_5.CO.CH_2.OC_2H_3O$ has been prepared by heating the chloride with alcoholic and potassium acetate. It crystallizes in large rhombic plates, melting at 44°, and boiling at 270°. Alcoholic potash converts it into *phenylglycolyl alcohol*, which has not been obtained in a pure state.

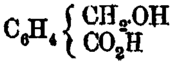
Phenylglycollic Acid, or *Mandelic Acid* $C_6H_5.CH(OH).CO_2H$, is produced by heating an alcoholic solution of oil of bitter almonds, prussic acid and hydrochloric acid for some time to 90°. It is readily soluble in water, and crystallizes in prisms. On heating it with hydriodic acid, it is reduced to phenylacetic acid, and oxidizing agents convert it into benzoic acid. Mandelic acid is isomeric with cresotic acid and tolyleneglycollic acid:—

Cresotic Acid.



$$C_6H_3\left\{\begin{matrix} OH \\ CH_3 \\ CO_2H \end{matrix}\right.$$

Tolyleneglycollic Acid.



$$C_6H_4\left\{\begin{matrix} CH_2.OH \\ CO_2H \end{matrix}\right.$$

Mandelic Acid.

$$C_6H_5.CH(OH)CO_2H$$

ETHENYL-BENZENE, OR STYROLENE $C_6H_5.C_2H_3$.

This hydrocarbon, which has also been called *phenyl-ethene*, occurs in the liquid styrax (from *Styrax officinalis*), and is isolated by distilling this balsam with a solution of sodium carbonate to retain cinnamic acid. It is also obtained by distilling cinnamic acid $C_6H_5.C_2H_2.CO_2H$ with baryta, and by heating styrolyl bromide with alkalis or distilling secondary styrolyl alcohol with zinc chloride. It appears to exist in coaltar, and is produced together with benzene and other bodies when acetylene is heated to a dull-red heat.

Styrolene is a mobile, very refractive, and fragrant liquid, boiling at 146°. When it is heated to 200°, it is converted into a polymeride, called *metastyrolene*; this transformation also takes place slowly at the ordinary temperature. By distillation it is reconverted into styrolene.

Distyrolene $C_{16}H_{16}$ is formed by heating styrolene with hydrochloric acid to 170°; it is an oily liquid, which on distillation does not yield styrolene.

The hydrocarbon existing in styrax is optically active, possessing a right-handed rotatory power; but that obtained from cinnamic acid is inactive. Styrolene is an aromatic olefine, and combines readily with the elements of the chlorine group.

Styrolene Dichloride $C_6H_5.C_2H_3Cl_2$ is a liquid which, on distilling it alone or with lime, is resolved into hydrochloric acid and *monochlorostyrolene* $C_6H_5.C_2H_2Cl$.

Styrolene Dibromide $C_6H_5.C_2H_3Br_2$ crystallizes in broad needles, possessing a pungent aromatic odour. It melts at 67°, and distils at 230°.

Styrolene Di-iodide $C_6H_5.C_2H_3I_2$ separates out in crystals on adding styrolene to a solution of iodine in potassium iodide. It is an unstable body, which easily decomposes into iodine and metastyrolene.

Nitrostyrolene $C_6H_4(NO_2)C_2H_3$ is formed by dissolving styrolene in fuming nitric acid. It crystallizes from alcohol in large prisms, possessing a pungent and aromatic odour.

ETHINYL-BENZENE, OR ACETENYL-BENZENE, $C_6H_5.C_2H$.

This hydrocarbon is formed by heating styrolene dibromide with an alcoholic potash-solution:—

$$C_6H_5.CHBr—CH_2Br = C_6H_5.C{\equiv}CH + 2HBr$$

It has also been obtained from methyl-phenyl ketone, by a reaction corresponding to the formation of allylene from dimethyl ketone. Phosphorus pentachloride converts the ketone into the dichloride $C_6H_5.CCl_2.CH_3$, which with alcoholic potash yields ethinyl-benzene.

It is a limpid and very refractive liquid, boiling at 140°, and possessing an aromatic odour. In its chemical properties it shows the greatest analogy to acetylene and allylene.

Sodium-ethinyl-benzene $C_6H_5.C_2Na$ is produced by adding sodium to an etherial solution of the hydrocarbon; it is a white powder, which in the air rapidly absorbs oxygen, and becomes red-hot, leaving a residue of carbon, and sodium carbonate. Water decomposes it into ethinyl-benzene, and caustic soda.

Silver-ethinyl-benzene $C_6H_5.C_2Ag$ is obtained as a light-grey precipitate by adding an alcoholic solution of the hydrocarbon to an ammoniacal silver-solution.

Copper-ethinyl-benzene $\left.\begin{matrix}C_6H_5C_2\\C_6H_5C_2\end{matrix}\right\}Cu_2$ is a yellow precipitate, produced by adding a very dilute alcoholic solution of ethinyl-benzene to an ammoniacal solution of cuprous chloride.

COMPOUNDS WITH NINE ATOMS OF CARBON.

The compounds of this group are derived from the following hydrocarbons:—

Trimethyl-benzenes $\left\{\begin{array}{l}\text{Mesitylene}\\ \text{Pseudocumene}\end{array}\right.$	$C_6H_2\left\{\begin{array}{l}CH_3\\ CH_3\\ CH_3\end{array}\right.$
Methyl-ethyl-benzene	$C_6H_4\left\{\begin{array}{l}CH_3\\ C_2H_5\end{array}\right.$
Propyl-benzene	$C_6H_5.C_3H_7$
Isopropyl-benzene or Cumene . .	$C_6H_5.CH\left\{\begin{array}{l}CH_3\\ CH_3\end{array}\right.$
Allyl-benzene	$C_6H_5.C_3H_5$

TRIMETHYL-BENZENES $C_6H_3(CH_3)_3$.

MESITYLENE, OR 1·3·5 TRIMETHYL-BENZENE

Occurs together with pseudocumene in coal-tar, and is produced by acting with sulphuric acid on acetone. Each molecule of this compound loses one molecule of water, and the residues $CH_3 - C—CH$ combine, three methyl-ethines being condensed to trimethyl-benzene, just as three molecules of ethine form one of benzene. (See page 318.) This reaction shows that the methyls occupy the symmetrical position 1·3·5.

Pure mesitylene is prepared by pouring one volume of acetone on some sand placed in a retort, and then adding a cold mixture of one volume of sulphuric acid and half a volume of water.

After 24 hours, the mixture is distilled, and the distillate purified by continued fractional distillation. Pure mesitylene is a refractive liquid, possessing a peculiar smell, and boiling at 163°.

Monochloromesitylene $C_6H_2Cl(CH_3)_3$ is a limpid liquid, boiling at 205°.

Dichloromesitylene $C_6HCl_2(CH_3)_3$ crystallizes from alcohol in shining prisms, melting at 59°, and boiling at 205°.

Trichloromesitylene $C_6Cl_3(CH_3)_3$ melts at 204°, and sublimes in long prisms.

These three compounds are formed by the action of chlorine on cold mesitylene.

Monobromomesitylene $C_6H_2Br(CH_3)_3$ is a liquid, boiling at 225°, and solidifying below 0°.

Dibromo- and *Tribromomesitylene* are crystalline solids; the former melting at 59°, and the latter at 244°.

Mononitromesitylene $C_6H_2(NO_2)(CH_3)_3$ is prodnced, together with mesitylenic acid, by heating mesitylene with common nitric acid. It crystallizes from alcohol in long, thick prisms, melting at 41°, and boiling between 240° to 250°.

Dinitromesitylene $C_6H(NO_2)_2(CH_3)_3$ is formed by dissolving the hydrocarbon in fuming nitric acid, and crystallizes in thin brilliant needles, melting at 86°.

Trinitromesitylene $C_6(NO_2)_3(CH_3)_3$ is obtained by acting on mesitylene with a mixture of concentrated nitric acid and sulphuric acid. It is sparingly soluble in alcohol, and crystallizes in needles, melting at 232°.

Amidomesitylene $C_6H_2(NH_2)(CH_3)_3$ is but slowly formed by boiling nitromesitylene with hydrochloric acid and tin. It is an oily liquid, and forms crystalline salts.

Diamidomesitylene $C_6H(NH_2)_2(CH_3)_3$ crystallizes from hot water in long, white needles, melting at 90°, and forms crystallizable salts.

Mesitylenesulphonic Acid $C_6H_2(CH_3)_3SO_3H$.—Mesitylene dissolves in warm fuming sulphuric acid, and on cooling the sulphonic acid crystallizes out in needles. By fusing it with caustic potash, it yields oxymesitylenic acid, and isoxylenol (see page 376).

Hexahydromesitylene $C_6H_9(CH_3)_3$ has been produced by heating mesitylene and phosphonium iodide gradually to 280°:—

$$C_6H_3(CH_3)_3 + 3PH_4I = C_6H_9(CH_3)_3 + 3PI$$

It is a liquid boiling at 136°, and smelling like petroleum. Oxidizing agents act on it but slowly, and fuming nitric acid converts it only on boiling into trinitromesitylene.

PSEUDOCUMENE, OR 1·3·4 TRIMETHYL-BENZENE.

This name was originally given to a liquid boiling at about 166°, which is obtained by the fractional distillation of coal-tar naphtha. Recent researches have, however, shown that this body is a mixture of mesitylene, and an isomeride for which the name pseudocumene has been retained.

Pure pseudocumene has been obtained by acting with sodium on a mixture of methyl iodide, and either bromo-isoxylene or bromomethyltoluene, from which it appears that the three methyls occupy the position 1·3·4.

Monobromopseudocumene $C_6H_2Br(CH_3)_3$ is formed by acting with bromine on well-cooled pseudocumene. It crystallizes from hot alcohol in thin plates, melting at 73°.

Dibromopseudocumene $C_6HBr_2(CH_3)_3$ is a heavy liquid, and *tribromopseudocumene* $C_6Br_3(CH_3)_3$ a solid, which is sparingly soluble in alcohol, and crystallizes in fine needles.

Mononitropseudocumene $C_6H_2(NO_2)(CH_3)_3$ is obtained by adding pseudocumene drop by drop to well-cooled, fuming nitric acid, and crystallizes from alcohol in colourless and very refractive prisms, melting at 71°, and boiling at 265°.

Dinitropseudocumene $C_6H(NO_2)_2(CH_3)_3$ is obtained in small quantity, together with the trinitro-compound, by heating mononitropseudocumene with concentrated nitric acid; it is a heavy, thick, yellow, oily liquid.

Trinitropseudocumene $C_6(NO_2)_3(CH_3)_3$ crystallizes from benzene in hard, transparent, square prisms, melting at 185°.

Amidopseudocumene $C_6H_2(NH_2)(CH_3)_3$.—When nitropseudocumene is heated with tin and hydrochloric acid, it dissolves, and, on cooling, shining plates of the double salt $C_6H_2(CH_3)_3NH_3Cl + SnCl_2$ crystallize out. By passing hydrogen sulphide through its aqueous solution, and evaporating the filtrate, *amidopseudocumene hydrochloride* is obtained in long prisms. The free base crystallizes from alcohol or hot water in silky needles, melting at 62°.

ACIDS DERIVED FROM THE TRIMETHYL-BENZENES.

Mesitylenic Acid $C_6H_3(CH_3)_2CO_2H$ is formed by boiling mesitylene with dilute nitric acid. It is sparingly soluble in water, but freely in alcohol, and crystallizes in plates, resembling benzoic acid, and melting at 166°. Calcium mesitylenate $2[(C_6H_3(CH_3)_2CO_2)_2Ca] + H_2O$ is as freely soluble in cold as in boiling water, and forms crystalline crusts; on distilling it with lime, it yields isoxylene.

Oxymesitylenic Acid $C_6H_2(CH_3)_2\left\{\begin{array}{l}OH\\CO_2H\end{array}\right.$ is formed by heating potassium mesitylenesulphonate with caustic potash to 250°:—

$$C_6H_2\left\{\begin{array}{l}SO_3K\\CH_3\\CH_3\\CH_3\end{array}\right. + 3KOH = C_6H_2\left\{\begin{array}{l}OK\\CH_3\\CH_3\\CO_2K\end{array}\right. + K_2SO_3 + 3H_2$$

It sublimes in dazzling white needles, melting at 176°, and gives a deep-blue colour with ferric chloride.

Uvitic Acid $C_6H_3(CH_3)\left\{\begin{array}{l}CO_2H\\CO_2H\end{array}\right.$.—This acid was first obtained by boiling pyruvic acid with baryta-water, and it is also produced by oxidizing mesitylene with nitric acid. It crystallizes from boiling water in fine needles, melting at 287°. On heating it with lime, it is resolved into carbon dioxide and toluene. Its nitrile has been obtained by heating potassium orthochlorotoluene-sulphonate with potassium cyanide.

Trimesitic Acid $C_6H_3\left\{\begin{matrix}CO_2H\\CO_2H\\CO_2H\end{matrix}\right.$ is obtained by oxidizing mesitylenic or uvitic acid with chromic acid-solution. It crystallizes from boiling water in hard, thick prisms, melting at 300°. *Normal barium mesitate* $[C_6H_3(CO_2)_3]_2Ba_3 + 2H_2O$ is a crystalline precipitate, which is almost insoluble in water. *Acid barium mesitate* $C_6H_3\left\{\begin{matrix}(CO_2)_2Ba\\CO_2H\end{matrix}\right. + 4H_2O$ is obtained in needles, by adding a solution of the acid to barium chloride; it is sparingly soluble in cold, and more freely in boiling water.

Xylic Acids $C_6H_3(CH_3)_2CO_2H$.—When pseudocumene is boiled with dilute nitric acid, two isomeric acids having this composition are formed. They are separated from the dibasic xylidic acid, which is formed at the same time, and nitro-products, by distilling repeatedly with water. The distillate is neutralized with sodium carbonate, and distilled to remove some nitropseudocumene, and the concentrated solution decomposed with hydrochloric acid. The acids are then converted into the calcium salts, which are separated by recrystallization, the xylate being much more soluble in water than the paraxylate.

Xylic acid is sparingly soluble in water, and crystallizes from alcohol in large prisms, melting at 126°. The same acid has been obtained by acting with carbon dioxide on a mixture of sodium and monobromo-isoxylene. By heating it with lime it yields isoxylene. These two reactions show that if the carboxyl has the position 1, the two methyls are in 2 and 4.

Chromic acid oxidizes xylic acid to carbon dioxide and acetic acid, no tribasic acid being formed.

Paraxylic Acid crystallizes from alcohol in large pointed prisms, melting at 163°. On heating it with lime, it is resolved into carbon dioxide and orthoxylene, showing that the two methyl-groups are in the position 3·4.

Xylidic Acid $C_6H_3\left\{\begin{matrix}CH_3\\CO_2H\\CO_2H\end{matrix}\right.$ is almost insoluble in water, and crystallizes from alcohol in granular nodules, melting at 291°, and subliming in hard needles.

ETHYL-METHYL-BENZENE $C_6H_4\left\{\begin{matrix}CH_3\\C_2H_5\end{matrix}\right.$.

This hydrocarbon has been obtained from parabromotoluene and methyl iodide. It is a liquid boiling at 159°, and yielding by oxidation paratoluic and terephthalic acids.

Ethylbenzoic Acid $C_6H_4\left\{\begin{matrix}CO_2H\\C_2H_5\end{matrix}\right.$ has been produced by oxidizing diethyl-benzene with dilute nitric acid, and by passing carbon dioxide into a mixture of ethyl-monobromobenzene and sodium. It crystallizes, like benzoic acid, in flat, brilliant needles, melting at 110°. Chromic acid oxidizes it to terephthalic acid.

Alphaxylic Acid $C_6H_4\left\{\begin{matrix}CH_3\\CH_2.CO_2H\end{matrix}\right.$—The nitrile of this acid is formed by heating tolyl chloride with potassium cyanide; by boiling it with caustic potash it yields the acid, crystallizing from boiling water in shining thin plates, melting at 42°.

PROPYL-BENZENE $C_6H_5.C_3H_7$

Has been prepared by acting with sodium on a mixture of propyl bromide and bromobenzene. It is a liquid boiling at 157°. On heating it with a mixture of sulphuric and nitric acids, it yields a liquid trinitro-compound; and with bromine it forms *propyl-tetrabromobenzene* $C_6HBr_4.C_3H_7$, a viscid liquid.

Phenylpropyl Alcohol $C_6H_5.C_3H_6.OH$ is found together with *cinnyl alcohol* $C_6H_5.C_3H_4.OH$ (see next page), and is also formed by acting with sodium-amalgam on an aqueous solution of the latter compound. It is a liquid boiling at 235°.

Phenylpropionic Acid $C_6H_5.C_2H_4.CO_2H$.—This compound is also called hydrocinnamic acid, because it was first obtained by acting with sodium-amalgam on an aqueous solution of *cinnamic acid* $C_6H_5.C_2H_2.CO_2H$. It is also produced by heating styrolyl chloride with potassium cyanide and alcohol, and boiling the solution with potash, and by oxidizing phenylpropyl alcohol with chromic acid. It crystallizes from boiling water in long, thin needles, melting at 47°, and boiling at 280°.

Paranitrophenylpropionic Acid $C_6H_4(NO_2)C_3H_5O_2$ is produced by dissolving phenylpropionic acid in very cold fuming nitric acid. It crystallizes from water in small, flat, brilliant needles, melting at 164°. Chromic acid oxidizes it to paranitrobenzoic acid.

Benzyl-methyl Ketone $C_6H_5.CH_2.CO.CH_3$ is a liquid boiling at 215°, which has been obtained by the action of zinc methide on the chloride of phenylacetic acid. Chromic acid oxidizes it to acetic acid and benzoic acid.

CUMENE, OR ISOPROPYL-BENZENE $C_6H_5.CH\left\{\begin{matrix}CH_3\\CH_3\end{matrix}\right.$

This hydrocarbon exists in Roman cumin-oil, and is obtained artificially by distilling *cumic acid* $C_6H_4(C_3H_7)CO_2H$ with lime. It boils at 151°, and gives, with nitric acid, a crystalline trinitro-compound;

and with excess of bromine it yields *pentrabromocumene,* crystallizing in fine needles, melting at 109°. Cumene has not yet been obtained synthetically; but as it yields benzoic acid by oxidation, and boils at a lower temperature than propyl-benzene, it must be isopropylbenzene, because isopropyl-compounds boil always at a lower temperature than the corresponding normal propyl-compounds.

ALLYL-BENZENE, OR PHENYL-PROPENE $C_6H_5.C_3H_5$.

This hydrocarbon is formed, together with phenylpropyl alcohol, by treating an aqueous solution of cinnyl alcohol with sodium-amalgam:—

$$C_6H_5{-}CH{=}CH{-}CH_2.OH + H_2 = C_6H_5{-}CH{=}CH{-}CH_3 + H_2O$$

It is a liquid boiling at about 170°, and yielding, with bromine, *phenyl-propene dibromide,* $C_6H_5.C_3H_5Br_2$, crystallizing from alcohol in large plates, melting at 66°·5.

Anethol or *Allylphenol-methyl Ether* $C_6H_4\left\{\begin{matrix}OCH_3\\C_3H_5\end{matrix}\right.$ is the principal constituent of oil of anise-seed and similar oils (see page 371), and crystallizes in soft shining scales, melting at 20°, and boiling at 225°. By heating it with solid caustic potash, it is resolved into methyl alcohol and *Anol,* or *Allyl-phenol,* $C_6H_4(OH)C_3H_5$, crystallizing in small shining plates; it distils with partial decomposition, and readily oxidizes in the air.

Eugenol, or *Eugenic Acid* $C_6H_3(OH)\left\{\begin{matrix}OCH_3\\C_3H_5\end{matrix}\right.$, exists in oil of cloves (*Caryophyllus aromaticus*), in oil of pimento (*Myrtus pimenta* and *M. communis*), and in the volatile oils of *Laurus nobilis, Persea caryophyllata,* and *Canella alba.* It is obtained by treating oil of cloves with caustic potash, which dissolves the eugenol, whilst a terpene $C_{10}H_{16}$ is left behind. By passing carbon dioxide in the filtered and boiled solution, eugenol is set free as a colourless and very refractive liquid, which soon assumes a brown colour. It boils at 253°, and possesses an aromatic odour and a very pungent and hot taste. When heated with strong hydriodic acid, it yields methyl iodide and a red resin $C_9H_{10}O_2$; and by fusing it with potash, it is resolved into acetic acid and protocatechuic acid.

CINNYL-COMPOUNDS.

Cinnyl Alcohol, or *Phenylallyl Alcohol* $C_6H_5.C_3H_4.OH$.—Liquid styrax (page 384) is a mixture of styrolene, cinnamic acid, the cinnamic ethers of phenylpropyl alcohol, and cinnyl alcohol and resins. To obtain cinnyl alcohol, the balsam is distilled with water to volatilize styrolene, and the residue boiled with a solution of sodium carbonate, which removes the cinnamic acid. The residue is treated with cold alcohol to dissolve the resins, and the remaining ethers are separated by crystallization from a mixture of alcohol and ether or benzene. The pure crystalline cinnyl cinnamate is boiled with concentrated caustic potash, and thus cinnyl alcohol is obtained, crystallizing in shining needles. It melts at 33°, boils at 250°, and possesses a fragrant odour like hyacinths.

Cinnyl Chloride $C_6H_5.C_3H_4Cl$ is obtained by heating the alcohol with hydrochloric acid. It is a heavy, oily liquid, which possesses an aromatic odour, and is decomposed by heat.

Cinnyl Iodide $C_6H_5.C_3H_4I$ is a similar body, and produced by treating the alcohol with iodine and phosphorus.

Cinnylamine $C_6H_5.C_3H_4.NH_2$ is obtained by the action of alcoholic ammonia on the chloride. It separates from ether in small crystals, which on heating volatilize in vapours, possessing an alkaline odour.

CINNAMYL-COMPOUNDS.

Cinnamaldehyde $C_6H_5.C_2H_2.COH$ is the chief constituent of oil of cinnamon (from *Persea Cinnamomum*) and oil of cassia (from *Persea Cassia*). It is produced artificially by oxidizing cinnyl alcohol with platinum-black in the presence of air, and by distilling a mixture of calcium cinnamate and formate. It has also been obtained by saturating a mixture of benzaldehyde and acetaldehyde with hydrochloric acid. This reaction is quite analogous to the formation of crotonaldehyde from acetaldehyde (page 267):—

$$C_6H_5.CHO + CH_3.COH = C_6H_5.CH{=}CH{-}COH + H_2O$$

Pure cinnamaldehyde is obtained by agitating oil of cassia with a concentrated solution of acid potassium sulphite; a crystalline magma is formed, which is pressed, dried, washed with dilute alcohol, and then decomposed with dilute sulphuric acid.

Cinnamaldehyde is a colourless, heavy, oily liquid, possessing a very fragrant odour. It volatilizes without decomposition only *in vacuo* or with steam. It absorbs readily oxygen, and is converted into cinnamic acid; dilute nitric and chromic acids oxidize it to benzaldehyde and benzoic acid.

Cinnamic Acid, or *Phenylacrylic Acid* $C_6H_5.C_2H_2.CO_2H$ exists in *styrax*, in balsam of Peru and Tolu, and in several kinds of gum-benzoin. It has been produced artificially by passing carbon dioxide into a mixture of monobromostyrolene and sodium, and by heating oil of bitter almonds with acetyl chloride:—

$$(1)\ C_6H_5.COH + CH_3.COCl = C_6H_5.CH{=}CH.COCl + H_2O$$

$$(2)\ C_6H_5.CH{=}CH.COCl + H_2O = C_6H_5.CH{=}CH.CO.OH + HCl$$

Cinnamic acid is generally prepared by distilling liquid styrax with a solution of sodium carbonate, and precipitating the filtered residual solution with hydrochloric acid. The precipitate is purified by crystallization or sublimation. It crystallizes from boiling water in fine needles, and from alcohol in transparent prisms, melting at 133°, and boiling at 300°. Its salts resemble the benzoates; ferric chloride produces in a neutral solution of a cinnamate a yellow precipitate.

Oxidizing agents convert it into benzaldehyde and benzoic acid, and nascent hydrogen combines with it, forming phenylpropionic acid (page 390).

When cinnamic acid is fused with caustic potash, it is resolved into acetic acid and benzoic or phenylformic acid, and when distilled with slaked lime it yields carbon dioxide and styrolene.

Ethyl Cinnamate $\left.\begin{matrix} C_6H_5.C_3H_2O \\ C_2H_5 \end{matrix}\right\}O$ is prepared by dissolving the acid in absolute alcohol, and passing hydrochloric gas into the solution. It is a fragrant, oily liquid, boiling at 267°.

Benzyl Cinnamate, or *Cinnamein* $\left.\begin{matrix} C_6H_5.C_3H_2O \\ C_6H_5.CH_2 \end{matrix}\right\}O$, occurs in balsam of Peru and Tolu, and has been prepared by sodium cinnamate with benzyl chloride. It crystallizes from alcohol in small, brilliant prisms, melting at 39°, and possessing an agreeable odour.

Cinnyl Cinnamate, or Styracin $\left.\begin{matrix} C_6H_5.C_3H_2O \\ C_6H_5.C_3H_4 \end{matrix}\right\}O$.—The preparation of this compound has already been described (page 391). It crystallizes in needles, melting at 50°, and possessing a fragrant odour.

Nitrocinnamic Acid $C_6H_4(NO_2)C_3H_3O_2$ exists in two modifications, which are formed by dissolving cinnamic acid in cold concentrated nitric acid.

Paranitrocinnamic Acid is but sparingly soluble in boiling alcohol, and crystallizes in small needles, melting at 265°. Chromic acid converts it into paranitrobenzoic acid.

Metanitrocinnamic Acid is more freely soluble in alcohol, and melts at 232°; on oxidation it yields metanitrobenzoic acid.

Phenyldibromopropionic Acid $C_6H_8.C_2H_2Br_2.CO_2H$ is readily formed by combining cinnamic acid with bromine. It crystallizes from alcohol in small rhombic plates, and yields, when heated with alcoholic potash, two isomeric monobromocinnamic acids.

Phenylpropiolic Acid $C_6H_5.C_2.CO_2H$ stands in the same relation to cinnamic acid as stearolic to oleic acid, and is obtained by boiling a monobromocinnamic acid with alcoholic potash, or by suspending sodium-ethenyl-benzene in ether, and passing carbon dioxide into it:—

$$C_6H_5.C{\equiv}CNa + CO_2 = C_6H_5.C{\equiv}C.CO_2Na$$

It crystallizes in white, silky needles, melting at 136°. It combines with two molecules of bromine or hydrogen, and is resolved by heating it with baryta into carbon dioxide and ethinyl-benzene.

PHENYL-LACTIC ACIDS.

Phenylchlorolactic Acid $C_6H_5.C_2H_2Cl(OH)CO_2H$ is formed by passing chlorine into a solution of sodium carbonate and cinnamate:—

$$C_6H_5.C_2H_2.CO_2H + ClOH = C_6H_5.C_2H_2\left\{\begin{matrix}Cl\\OH\\CO_2H\end{matrix}\right.$$

It crystallizes from water in small hexagonal plates, containing one molecule of water.

Phenylbromolactic Acid $C_6H_5.C_2H_2Br(OH)CO_2H$ is a very similar compound, which is obtained, together with hydrobromic acid and some bromostyrolene and carbon dioxide, when phenyldibromopropionic acid is boiled with water:—

$$C_6H_5.C_2H_2Br_2.CO_2H + H_2O = C_6H_5.C_2H_2Br(OH)CO_2H + HBr$$

Phenyl-lactic Acid $C_6H_5.C_2H_3(OH)CO_2H$.—When either of the preceding compounds is treated with water and sodium-amalgam until hydrogen is briskly evolving, they are converted into phenyl-lactic acid, which is isolated by neutralizing the solution with hydrochloric acid, and evaporating it on a water-bath. The residue is acidulated with hydrochloric acid and shaken with ether. On evaporation the etherial solution, impure phenyl-lactic acid, is left behind, which is crystallized from hot water. It forms flat, pointed needles, melting at 94°, and is resolved at 180° into water and cinnamic acid. By heating it with hydrobromic or hydrochloric acid, the hydroxyl is again replaced by bromine or chlorine.

Phenylparalactic Acid, or *Tropic Acid* $C_6H_5.CH\left\{\begin{matrix}CH_2.OH\\CO_2H\end{matrix}\right.$, has been obtained by heating atropine (see Alkaloids) gently with baryta-water, or by leaving it in contact with fuming hydrochloric acid. From a hot aqueous solution it separates in slender prisms, melting at 118°.

Atropic Acid $C_6H_5.C_2H_2.CO_2H$ is formed when tropic acid is heated with concentrated baryta-water to 136°. It crystallizes from water in needles, and from alcohol in plates, melting at 106°·5, and possessing an aromatic, pungent smell, like benzoic acid. Chromic acid oxidizes it to benzoic acid; and, by fusing it with potash, it is resolved into formic acid and phenylacetic acid (while the isomeric cinnamic acid yields acetic acid and phenyl-formic acid):—

$$C_6H_5.\underset{\displaystyle CO_2H}{\overset{\displaystyle CH_2}{\overset{\|}{\underset{|}{C}}}} + 2KOH = C_6H_5.CH_2—CO_2K + CHKO_2 + H_2$$

It combines with one molecule of bromine, and with nascent hydrogen, forming oily *hydratopic acid* $C_6H_5.CH\left\{\begin{matrix}CH_3\\CO_2H.\end{matrix}\right.$

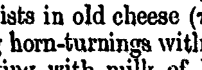
Isatropic Acid is isomeric, or probably polymeric, with atropic acid, and formed together with the latter, when tropic acid is heated with hydrochloric acid to 140°. It is sparingly soluble in boiling water, and less freely in alcohol than atropic acid, and forms microscopic, monoclinic crystals, melting only at about 200°. It does not combine with nascent hydrogen.

OXYPHENYL-PROPIONIC ACIDS.

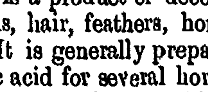
Phloretic Acid $C_6H_4\left\{\begin{matrix}OH\\C_2H_4.CO_2H\end{matrix}\right.$ is a product of decomposition of phloretin (see Glucosides), and crystallizes from boiling water in brittle, prismatic crystals, melting at 130°. When heated with baryta, it splits up into carbon dioxide and phlorol (page 382). On fusing it with potash, it yields para-oxybenzoic acid.

Hydroparacumaric Acid $C_6H_4\left\{\begin{matrix}OH\\C_2H_4.CO_2H\end{matrix}\right.$ has been obtained by reducing paranitrophenylpropionic acid with tin and hydrochloric acid, and converting the amido-acid into a diazo-compound, which, when boiled with water, yields oxyphenylpropionic acid. It crystallizes from water in small, monoclinic prisms, melting at 125°, and yields by oxidation para-oxybenzoic acid.

As both phloretic and hydroparacumaric acid are so easily converted into para-oxybenzoic acid, they contain the two side-chains in the position 1·4, and their isomerism must be caused by the group $C_6H_4.OH$ replacing different hydrogen atoms in propionic acid, thus:



$$\begin{matrix} & C_6H_4.OH & \\ & | & \\ H_3C- & CH & -CO_2H\end{matrix}$$



$$\begin{matrix}C_6H_4.OH & \\ | & \\ H_2C & -CH_2-CO_2H\end{matrix}$$

Tyrosine, or *Oxyphenylamidopropionic Acid* $C_6H_4\left\{\begin{matrix}OH\\C_2H_3(NH_2)CO_2H\end{matrix}\right.$ is either a derivative of phloretic acid or of parahydrocumaric acid. It has not been obtained by synthesis, but is a product of decomposition of animal substances, such as proteids, hair, feathers, horn, &c., and exists in old cheese (τυρός, cheese). It is generally prepared by boiling horn-turnings with dilute sulphuric acid for several hours, and saturating with milk of lime. By adding hydrochloric acid to the concentrated solution, tyrosine is precipitated, while leucine (page 234) remains in solution.

Tyrosine is sparingly soluble in cold water and alcohol, and crystallizes from hot water in slender needles. Tyrosine is a phenol, and at the same time possesses, like other amido-acids, the properties of a base and an acid. By dry distillation, it yields phenol and other products; but, when heated very carefully, it is resolved into carbon dioxide and *oxyphenyl-ethylamine* $C_6H_4(OH)C_2H_4.NH_2$, a white, crystalline sublimate, having an alkaline reaction, and forming crystallizable salts. When tyrosine is fused with potash, it yields ammonia, acetic acid, and paraoxybenzoic acid; and when heated with hydriodic acid, it is resolved into ethyl-phenol (or an isomeride), carbon dioxide, and ammonia:—

$$C_6H_4\left\{\begin{matrix}OH\\ C_2H_2\left\{\begin{matrix}NH_2\\ CO_2H\end{matrix}\right.\end{matrix}\right. + 2HI = C_6H_4\left\{\begin{matrix}OH\\ C_2H_5\end{matrix}\right. + CO_2 + NH_3 + I_2$$

Tyrosine dissolves in hot sulphuric acid, yielding sulpho-acids, which are coloured violet by ferric chloride. On heating an aqueous solution of tyrosine with mercurious nitrate, it assumes a red colour, and then a reddish-brown precipitate is formed.

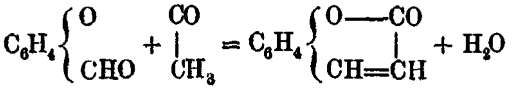
Melilotic Acid, or *Hydrocumaric Acid* $C_6H_4\left\{\begin{matrix}OH\\ C_2H_4.CO_2H\end{matrix}\right.$, occurs in the yellow melilot (*Melilotus officinalis*), and in the fragrant Faham-leaves. It crystallizes from water in large, pointed prisms, melting at 82°. By distillation it is resolved into water and *melilotic anhydride* $C_6H_4\left\{\begin{matrix}O\\ C_2H_4\end{matrix}\right.>CO$, a crystalline solid, melting at 25°, and boiling at 272°. On fusing melilotic acid with potash, it yields acetic acid and salicylic acid.

OXYPHENYL-ACRYLIC ACIDS.

Paracumaric Acid $C_6H_4\left\{\begin{matrix}OH\\ C_2H_2.CO_2H\end{matrix}\right.$ is prepared by exhausting aloes with dilute sulphuric acid, and treating the residne with ether. It crystallizes from boiling water in brittle needles, melting at 180°. Nascent hydrogen converts it into hydroparacumaric acid.

Cumaric Acid $C_6H_4\left\{\begin{matrix}OH\\ C_2H_2.CO_2H\end{matrix}\right.$ occurs together with melilotic acid, and crystallizes from water in long needles, melting at 195°; by treating it with water and sodium-amalgam, it is converted into melilotic acid.

Cumarin, or *Cumaric Anhydride* $C_6H_4\left\{\begin{matrix}O\\ C_2H_2\end{matrix}\right.>CO$, is found, combined with cumaric acid or melilotic acid, in the melilot and the Faham-leaves, and exists in the free state in the Tonka-bean (*Dipterix odorata*), in the sweet woodruff (*Asperula odorata*), and in the sweet-scented vernal grass (*Anthoxanthum odoratum*). It is readily obtained by exhausting tonka-beans with alcohol; and has been produced artificially by heating sodium-salicylaldehyde with acetic anhydride, sodium acetate being formed, and acetyl is set free, which combines with the aldehyde-residue with the elimination of water:—

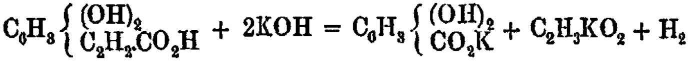


$$C_6H_4\left\{\begin{matrix}O\\ CHO\end{matrix}\right. + \begin{matrix}CO\\ |\\ CH_3\end{matrix} = C_6H_4\left\{\begin{matrix}O—CO\\ \quad |\\ CH=CH\end{matrix}\right. + H_2O$$

Cumarin is sparingly soluble in cold water, more freely in alcohol and boiling water, and crystallizes in large transparent prisms, possessing a very fragrant odour. It melts at 67°, and boils at 291°. By heating it with potash and a little water, it is converted into potassium cumarate, and sodium-amalgam and water transform it into melilotic acid.

By acting on sodium-salicylaldehyde with butyric or valerianic anhydride, homologues of cumarin are formed, which also possess a fragrant smell.

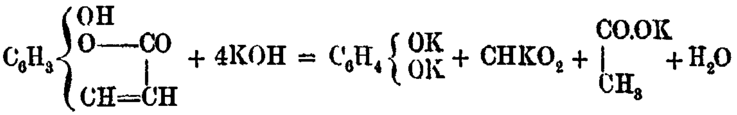
Caffeic Acid $C_6H_3\left\{\begin{matrix}(OH)_2\\ C_2H_2.CO_2H\end{matrix}\right.$ occurs as glucoside, called caffeetannic acid, in coffee, and is conveniently prepared by boiling coffee-extract with caustic potash. It is sparingly soluble in cold water, and crystallizes from boiling water in small, glistening plates. On heating, it yields pyrocatechin; and by fusing it with potash, it is resolved into acetic acid and protocatechuic acid:—



$$C_6H_3\left\{\begin{matrix}(OH)_2\\ C_2H_2.CO_2H\end{matrix}\right. + 2KOH = C_6H_3\left\{\begin{matrix}(OH)_2\\ CO_2K\end{matrix}\right. + C_2H_3KO_2 + H_2$$

Hydrocaffeic Acid $C_6H_3\left\{\begin{matrix}(OH)_2\\ C_2H_4.CO_2H\end{matrix}\right.$ is formed by adding sodium-amalgam to a hot solution of caffeic acid; it crystallizes from water in rhombic prisms. Its aqueous solution gives, with ferric chloride, an intensely green colour, which changes into cherry-red by adding sodium carbonate. Caffeic acid gives a similar reaction.

Umbelliferon $C_9H_6O_3$ exists in the bark of the mezereon, and is also produced by the dry distillation of galbanum, and similar gum-resins. From boiling water it crystallizes in rhombic prisms, melting at 240°. It contains one hydroxyl, the hydrogen of which is easily replaced by acid radicals. Concentrated boiling potash resolves it into formic acid, acetic acid, and resorcin. It appears, therefore, to be a oxycumarin:—



$$C_6H_3\left\{\begin{matrix}OH\\ O—CO\\ \quad |\\ CH=CH\end{matrix}\right. + 4KOH = C_6H_4\left\{\begin{matrix}OK\\ OK\end{matrix}\right. + CHKO_2 + \begin{matrix}CO.OK\\ |\\ CH_3\end{matrix} + H_2O$$

Umbellic Acid $C_6H_3(OH_2)C_2H_4.CO_2H$ is produced by adding sodium-amalgam to a hot solution of umbelliferon. It forms granular crystals, melting at 125°. Its aqueous solution is coloured green by ferric chloride.

Veratric Acid $C_8H_7(OH_2)CO_2H$.—This isomeride of hydrocaffeic and umbellic acids exists in sabadilla-seed (*Veratrum Sabadilla*), and crystallizes from boiling water in prisms. When heated with caustic baryta, it is resolved into carbon dioxide and *veratrol* $C_8H_8(OH)_2$, a colourless oil, possessing an aromatic odour, boiling at 205°, and solidifying at 15° to a crystalline mass.

Veratrol is either a dimethyl-dioxybenzene or an ethyl-dioxybenzene.

COMPOUNDS WITH TEN ATOMS OF CARBON.

We know the following hydrocarbons belonging to this group:—

Tetramethyl-benzene	$C_6H_2\left\{\begin{matrix}CH_3\\CH_3\\CH_3\\CH_3\end{matrix}\right.$
Dimethyl-ethyl-benzene . . .	$C_6H_3\left\{\begin{matrix}CH_3\\C_2H_5\\CH_3\end{matrix}\right.$
Methyl-propyl-benzene . . .	$C_6H_4\left\{\begin{matrix}CH_3\\C_3H_7\end{matrix}\right.$
Methyl-isopropyl-benzene . .	$C_6H_4\left\{\begin{matrix}CH_3\\CH(CH_3)_2\end{matrix}\right.$
Diethyl-benzene	$C_6H_4\left\{\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right.$
Isobutyl-benzene	$C_6H_5.C_2H_3(CH_3)_2$
Butenyl-benzene	$C_6H_5.C_4H_7$

Tetramethyl-benzene, or Durene $C_6H_2(CH_3)_4$.—This hydrocarbon does not exist in coal-tar, but has been obtained artificially by the action of sodium on a solution of methyl iodide and monobromopseudocumene in pure ether. Durene is the only homologue of benzene which is solid at the ordinary temperature (*durus*, hard), and crystallizes from alcohol in compact, oblique prisms, melting at 80°, and boiling at 190°. It is lighter than water, and possesses a faint odour resembling that of benzene.

Dinitrodurene $C_6(NO_2)_2(CH_3)_4$ is formed by dissolving durene in cold concentrated nitric acid, and crystallizes from alcohol in colourless, rhombic prisms, melting at 205°, and subliming in brilliant needles.

Dibromodurene $C_6Br_2(CH_3)_4$ is obtained by the action of cold bromine on durene, and is but sparingly soluble in boiling alcohol.

It forms long, slender, silky needles, melting at 199°, and subliming without decomposition.

Cumylic Acid $C_6H_2\left\{\begin{matrix}(CH_3)_3\\CO_2H\end{matrix}\right.$.—This monobasic acid has been prepared by boiling durene with dilute nitric acid. It is very sparingly soluble in water, and crystallizes from an alcoholic solution in hard, glistening needles or brilliant prisms, melting at 150°. It easily volatilizes, and sublimes in slender needles.

Cumidic Acid $C_6H_2\left\{\begin{matrix}(CH_3)_2\\(CO_2H)_2\end{matrix}\right.$ is formed, together with cumylic acid. It is but sparingly soluble in water, and scarcely in benzene; and is obtained in long, transparent prisms by adding benzene to its alcoholic solution. It sublimes at a high temperature without previously melting.

DIMETHYL-ETHYL-BENZENE, OR ETHYL-ISOXYLENE $C_6H_3\left\{\begin{matrix}(CH_3)_2\\C_2H_5\end{matrix}\right.$

Has been obtained by acting with sodium on a mixture of ethyl bromide and monobromo-isoxylene. It is a colourless liquid, boiling at 184°.

DIETHYL-BENZENE $C_6H_4(C_2H_5)_2$

Is formed by acting with sodium on ethyl bromide and ethyl-monobromobenzene. It boils at 179°, and yields, on oxidation, ethylbenzoic acid and terephthalic acid.

METHYL-PROPYL-BENZENE $C_6H_4\left\{\begin{matrix}C_3H_7\\CH_3\end{matrix}\right.$.

This compound is formed by the action of sodium on a mixture of 1·4 bromotoluene and propyl bromide. It boils at 179°, and yields thick, oily nitro-compounds. Dilute nitric and chromic acid oxidize it to paratoluic acid and terephthalic acid.

CYMENE, OR METHYL-ISOPROPYL-BENZENE $C_6H_4\left\{\begin{matrix}CH_3\\CH(CH_3)_2\end{matrix}\right.$.

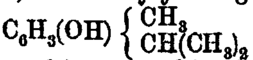
Cymene has not been produced by synthesis, but occurs, together with cumic aldehyde, in Roman cumin-oil (*Cuminum Cyminum*), and in the oil of the water-hemlock (*Cicuta virosa*), and mixed with thymol and a terpene in oil of thyme (*Thymus vulgaris*), and the oils of *Ptychotis Ajowan*, and *Monarda punctata*, and other volatile oils.

Cymene has been obtained by abstracting two atoms of hydrogen from oil of turpentine (page 301), and is most conveniently prepared by distilling camphor with phosphorus pentasulphide:—

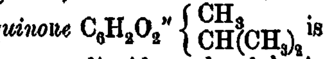
$$5C_{10}H_{16}O + P_2S_5 = 5C_{10}H_{14} + 5SH_2 + P_2O_5$$

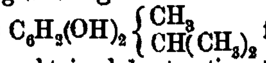
The product is washed with soda-solution, and distilled over sodium.

Cymene is a colourless, refractive liquid, possessing an aromatic smell, and boiling at 175°. It yields the same oxidation-products as methyl-propyl-benzene, but differs from it, not only by its lower boiling-point, but also by yielding crystalline nitro-products.

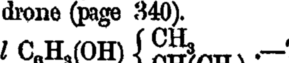
Thymol  $C_6H_3(OH)\left\{\begin{array}{l}CH_3\\CH(CH_3)_2\end{array}\right.$ occurs in the above-mentioned volatile oils, and is prepared by shaking oil of thyme with soda-solution, and decomposing the liquid, after the hydrocarbons have been removed, by hydrochloric acid.

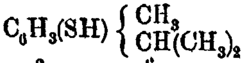
Thymol crystallizes in rhombic plates, melting at 44°, and boiling at 230°. It possesses a peppery taste and the odour of thyme. Phosphorus pentoxide resolves it into 1·3 cresol and propene, and phosphorus pentachloride converts it into *monochlorocymene* $C_6H_3Cl(CH_3)CH(CH_3)_2$, which, by acting with sodium-amalgam on its slightly acid, alcoholic solution, is transformed into cymene.

Thymoquinone  $C_6H_2O_2''\left\{\begin{array}{l}CH_3\\CH(CH_3)_2\end{array}\right.$ is produced by oxidizing thymol with manganese dioxide and sulphuric acid; it forms yellow prismatic plates, possessing a strong aromatic odour.

Thymohydroquinone  $C_6H_2(OH)_2\left\{\begin{array}{l}CH_3\\CH(CH_3)_2\end{array}\right.$ forms colourless, transparent needles, and is obtained by treating the quinone with sulphurous acid.

Both compounds readily combine, and form *thymoquinhydrone*, which crystallizes in black, shining needles, and has a constitution analogous to that of quinhydrone (page 340).

Oxycymene, or *Cymophenol*  $C_6H_3(OH)\left\{\begin{array}{l}CH_3\\CH(CH_3)_2\end{array}\right.$.—This isomeride of thymol has been obtained by dissolving cymene in sulphuric acid, and fusing the product with potash. It is also produced by the action of iodine on camphor. Cymophenol is a thick, colourless oil, which does not solidify at a low temperature, and smells like Russian leather.

Thiocymene  $C_6H_3(SH)\left\{\begin{array}{l}CH_3\\CH(CH_3)_2\end{array}\right.$ is formed as a by-product in the preparation of cymene from camphor, and has been also obtained by distilling oxycymene with phosphorus pentasulphide, and by converting potassium cymenesulphonate by means of phosphorus pentachloride into *cymenesulphonic chloride* $C_6H_3(SO_2Cl)(CH_3)CH(CH_3)_2$, and reducing the latter with nascent hydrogen.

Thiocymene is a colourless liquid, boiling at 235°, and possessing an aromatic smell. Oxidizing agents convert it first into the disulphide $(C_{10}H_{13})_2S_2$, a heavy, yellow oil, which by further oxidation yields a *sulphotoluic acid* $C_6H_3\left\{\begin{matrix}CH_3\\CO_2H\\SO_3H\end{matrix}\right.$.

CYMYL- AND CUMINYL-COMPOUNDS.

By treating boiling cymene with chlorine, substitution takes place in one of the alcohol-radicals, and *cymyl chloride* is formed, which, by heating with an alcoholic solution of potassium acetate, is converted into *cymyl acetate*, an oily liquid, boiling at 230°, and smelling like rose-wood.

Cymyl Alcohol $C_6H_4\left\{\begin{matrix}CH_2.OH\\C_3H_7\end{matrix}\right.$ is produced, together with cumic acid, by the action of alcoholic potash on cuminaldehyde. It is an aromatic liquid, boiling at 243°.

Cuminaldehyde, or *Cuminol* $C_6H_4\left\{\begin{matrix}COH\\C_3H_7\end{matrix}\right.$, occurs, together with cymene, in Roman cumin-oil and the oil of the water-hemlock, and is obtained pure by shaking the oil with a concentrated solution of acid potassium sulphite, and distilling the crystalline compound thus formed with sodium carbonate.

It is a liquid possessing a strong aromatic odour, and boiling at 237°. By fusing it with potash, it is converted into cumic acid:—

$$C_6H_4\left\{\begin{matrix}COH\\C_3H_7\end{matrix}\right. + KOH = C_6H_4\left\{\begin{matrix}CO.OK\\C_3H_7\end{matrix}\right. + H_2$$

Chromic acid oxidizes it to terephthalic acid.

Cumic Acid $C_6H_4\left\{\begin{matrix}CO.OH\\C_3H_7\end{matrix}\right.$ is sparingly soluble in water, and freely in alcohol, and forms prismatic plates, melting at 113°. When cymene is taken internally, it appears in the urine as cumic acid.

By distillation with quicklime, it is resolved into carbon dioxide and cumene (page 390).

Nitrocumic Acid $C_6H_3(NO_2)(C_3H_7)CO_2H$ forms yellow scales, and yields by reduction *amidocumic acid* $C_6H_3(NH_2)(C_3H_7)CO_2H$, crystallizing from hot water in colourless plates. By distillation with baryta, it is resolved into carbon dioxide and *cumidine*, or *isopropyl-amidobenzene* $C_6H_4\left\{\begin{matrix}NH_2\\C_3H_7\end{matrix}\right.$. By passing nitrogen trioxide into an aqueous solution of amidocumic acid, it is converted into *oxycumic acid* $C_6H_3(OH)\left\{\begin{matrix}CO_2H\\C_3H_7\end{matrix}\right.$, crystallizing from hot water in small prisms.

Oxy-isopropyl-phenyl-formic Acid $C_6H_4\left\{\begin{matrix}CO_2H\\C_3H_6OH\end{matrix}\right.$.—When cumic acid is heated with bromine and fuming hydrobromic acid, one atom of hydrogen in the isopropyl-group is replaced by bromine, and by boiling the product with alcoholic potash the oxy-acid is formed, which is isomeric with oxycumic acid, the latter being at the same time a phenol, while the former, as alcohol, is an aromatic glycollic acid.

Eugetic Acid $C_6H_2(OH)\left\{\begin{array}{l}C_3H_5\\OCH_3\\CO_2H\end{array}\right.$ is produced by acting with carbon dioxide and sodium on eugenol (page 390). It forms colourless prisms, melting at 124°. It is only sparingly soluble in water; the solution is coloured deep-blue by ferric salts. By dry distillation, it is resolved into eugenol and carbon dioxide.

ISOBUTYL-BENZENE $C_6H_5.C_2H_3(CH_3)_2$.

This compound is a refractive liquid, boiling at 160°, and possessing a fragrant odour. It has been obtained by the action of sodium, on a mixture of bromobenzene and isobutyl bromide. With bromine and nitric acid, it forms thick, oily substitution-products, which are decomposed by heat.

BUTENYL-BENZENE $C_6H_5.C_4H_7$.

This hydrocarbon, which is also called *phenylbutene*, is prepared by adding sodium to a mixture of benzyl chloride, allyl iodide, and ether:—

$$C_6H_5.CH_2Cl + C_3H_5I + Na_2 = C_6H_5.CH_2.C_3H_5 + NaCl + NaI.$$

It is a limpid liquid, boiling at 177°, and possessing a strong aromatic smell. It readily combines with one molecule of bromine.

Phenylethenyl-methyl Ketone, or *Acetocinnamone* $C_6H_5.C_2H_2.CO.CH_3$, is obtained by distilling a mixture of calcium cinnamate and acetate. It is a fragrant liquid, boiling at 240°. By the action of sodium amalgam on its alcoholic solution, it is converted into *phenylethyl-methyl carbinol* $\left.\begin{array}{c}C_6H_5.C_2H_4\\CH_3\end{array}\right\}CH.OH$, a crystalline solid, which is isomeric with the oxycymenes and with cymyl alcohol.

COMPOUNDS WITH ELEVEN ATOMS OF CARBON.

Amyl-benzene $C_6H_5.C_5H_{11}$ is produced by the action of sodium on a mixture of bromobenzene, amyl bromide, and benzene. It is a liquid boiling at 193°; with nitric acid it forms a yellow, oily mononitro-compound, and chromic acid oxidizes it to benzoic acid and isobutyric acid.

Diethyl-benzylene $C_6H_5.CH(C_2H_5)_2$ has been obtained by adding zinc ethide to a solution of benzylene chloride in benzene. It is a fragrant liquid, boiling at 178°.

Phenyl-angelic Acid $C_6H_5.C_4H_6.CO_2H$.—This homologue of cinnamic acid has been produced by heating benzaldehyde with butyryl chloride to 130°. It crystallizes from hot water in long needles, melting at 81°.

Homocumic, or *Cymic Acid* $C_6H_4\left\{\begin{array}{l}CH_2CO_2H\\C_3H_7\end{array}\right.$.—The nitrile of this acid is formed by converting cymyl alcohol into the chloride, and heating it with potassium cyanide. By boiling the nitrile with alcoholic potash, the acid is obtained; it forms small needles, melting at 52°.

Thymotic Acid $C_6H_2(OH)\left\{\begin{array}{l}CO_2H\\CH_3\\C_3H_7\end{array}\right.$ is produced by acting with sodium and carbon dioxide on thymol. It forms slender needles, melting at 120°, and subliming with decomposition. Its aqueous solution is coloured deep-blue by ferric chloride. By distillation with baryta, it is resolved into thymol and carbon dioxide.

COMPOUNDS WITH TWELVE ATOMS OF CARBON.

Amyl-toluene $C_6H_4\left\{\begin{array}{l}CH_3\\C_5H_{11}\end{array}\right.$ is a liquid boiling at 213°, which is formed by adding sodium to a mixture of amyl bromide and bromotoluene.

MELLITIC ACID $C_{12}H_6O_{12}$.

The mineral *Mellite*, or *Honey-stone*, which is found in deposits of lignite, is the aluminium salt of this acid. The free acid is obtained by boiling the finely-powdered mineral with water and ammonium carbonate, and concentrating the solution. Ammonium mellitate crystallizes out, which is boiled with baryta-water until all ammonia is expelled, and the pure barium salt is decomposed with sulphuric acid. The ammonium salt may also be precipitated with silver-nitrate, and the precipitate decomposed by hydrochloric acid.

Mellitic acid has also been produced, together with oxalic acid and other bodies, by oxidizing pure charcoal with an alkaline solution of potassium permanganate.

Mellitic acid is readily soluble in water and alcohol, and crystallizes in colourless needles, possessing a strong sour taste. It is a very stable body, which is not acted upon by hot concentrated sulphuric acid or nitric acid, nor by bromine or hydriodic acid. By distilling it with quicklime, it is resolved into benzene and carbon dioxide:—

$$C_{12}H_6O_{12} = C_6H_6 + 6CO_2$$

It is consequently *hexacarboxybenzene* $C_6(CO_2H)_6$, or the last term of a series of acids, which are derived from benzene by replacing one atom of hydrogen after the other by carboxyl, and all of which are resolved by heating them with lime into carbon dioxide and benzene.

Ammonium Mellitate $C_6(CO_2NH_4)_6 + 9H_2O$ forms large rhombic prisms.

Barium Mellitate $C_6(CO_2)_6Ba_3 + 3H_2O$ is obtained by adding barium chloride to a solution of the barium salt as a white precipitate, which soon changes into small plates.

Aluminium Mellitate $C_6(CO_2)_6Al_2 + 18H_2O$ exists as honey-stone in large, yellow, square octahedrons.

Silver Mellitate $C_6(CO_2Ag)_6$ is a white crystalline precipitate, which by heat is resolved into metallic silver and carbon monoxide.

Besides these normal salts, there exist also salts, containing two metals and acid salts:—

$$C_6\left\{\begin{matrix}(CO_2H)_4\\(CO_2NH_4)_2\end{matrix}\right. \quad C_6\left\{\begin{matrix}(CO_2H)_3\\(CO_2K)_3\end{matrix}\right. \quad C_6\left\{\begin{matrix}(CO_2H)_2\\(CO_2)_4Cu_2\end{matrix}\right. \quad C_6\left\{\begin{matrix}(CO_2NH_4)_2\\(CO_2)_4Cu_2\end{matrix}\right.$$

Ethyl Mellitate $C_6(CO_2.C_2H_5)_6$ is obtained by the action of ethyl iodide on the silver salt, and forms large colourless crystals, melting at 69°.

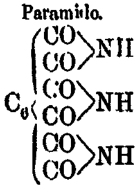
Mellitic Chloride $C_6(COCl)_6$ is formed by heating the acid with phosphorus pentachloride. It is a crystalline mass, which is slowly dissolved by boiling water, with the formation of hydrochloric acid and mellitic acid.

Mellimide, or *Paramide* $C_{12}H_3N_3O_6$ is produced, together with ammonia and the ammonium salt of euchroic acid, by heating ammonium mellitate. It is a white, amorphous powder, which is insoluble in water and alcohol, and is converted into acid ammonium mellitate $C_6(CO_2H)_3(CO_2NH_4)_3$ by heating it with water to 200°.

Euchroic Acid $C_{12}H_4N_2O_8$ forms colourless prisms, which are sparingly soluble in water. By the action of zinc or other reducing agents, it is converted into a deep-blue, insoluble substance, called *euchrone*, which dissolves in alkalis with a deep-purple colour, and in contact with air is oxidized again to euchroic acid. When euchroic acid is heated with water to 200°, it yields the acid salt $C_6(CO_2H)_4(CO_2NH_4)_2$.

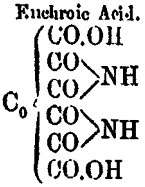
The constitution of these bodies is explained by the following formulæ:—

Paramide.



$$C_6\begin{cases}\begin{matrix}CO\\CO\end{matrix}>NH\\\begin{matrix}CO\\CO\end{matrix}>NH\\\begin{matrix}CO\\CO\end{matrix}>NH\end{cases}$$

Euchroic Acid.



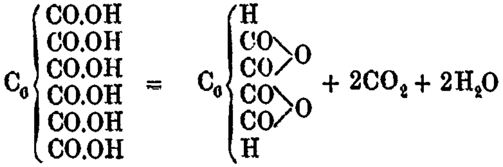
$$C_6\begin{cases}CO.OH\\\begin{matrix}CO\\CO\end{matrix}>NH\\\begin{matrix}CO\\CO\end{matrix}>NH\\CO.OH\end{cases}$$

Hydromellitic Acid $C_6H_6(CO_2H)$.—This additive compound is readily formed by the action of sodium-amalgam on an ammoniacal solution of mellitic acid. To isolate the acid, the solution is neutralized with acetic acid, and precipitated with lead acetate, the precipitate washed and decomposed with hydrogen sulphide. On evaporating the filtrate, the acid is obtained as a syrupy liquid, which gradually becomes crystalline.

Isohydromellitic Acid $C_6H_6(CO_2H)_6$ is obtained by heating hydromellitic acid with concentrated hydrochloric acid to 180°. It crystallizes in thick, large, four-sided prisms, possessing a slightly acid taste.

Isohydromellitic acid is a very stable body, which is not changed by treating it with a mixture of strong sulphuric and nitric acids. The cause of the isomerism of hydromellitic acid and isohydromellitic acid is not known.

Pyromellitic Acid $C_6H_2(CO_2H)_4$.—When mellitic acid is heated it first melts, and then is resolved into water, carbon dioxide, and *pyromellitic anhydride*:—



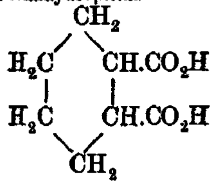
$$C_6\begin{cases}CO.OH\\CO.OH\\CO.OH\\CO.OH\\CO.OH\\CO.OH\end{cases} = C_6\begin{cases}H\\\begin{matrix}CO\\CO\end{matrix}>O\\\begin{matrix}CO\\CO\end{matrix}>O\\H\end{cases} + 2CO_2 + 2H_2O$$

The anhydride sublimes in long needles, and readily dissolves in warm water, forming pyromellitic acid, which crystallizes in prisms, and has great resemblance to phthalic acid. By the action of sodium-amalgam and water, it is slowly converted into two isomeric acids $C_6H_6(CO_2H)_4$. One of them, called *hydropyromellitic acid*, is a gummy mass; while *isohydropyromellitic acid* crystallizes from water in needles. On heating either of these acids above 200°, it is resolved into water, carbon dioxide, and *tetrahydrophthalic anhydride*, which readily combines with water, *tetrahydrophthalic acid* $C_6H_8(CO_2H)_2$ being formed, crystallizing from water in large plates, melting at 100°.

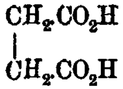
When this compound is heated with concentrated hydriodic acid to 230°, it is converted into *hexahydrophthalic acid* $C_6H_{10}(CO_2H)_2$, which has also been obtained from phthalic acid. By adding bromine to an aqueous solution of tetrahydrophthalic acid, it yields *bromomalophthalic acid* $C_6H_8Br(OH)(CO_2H)_2$, which by the action of baryta-water is converted into *tartrophthalic acid* $C_6H_8(OH)_2(CO_2H)_2$, crystallizing from water in large prisms. By heating it with hydriodic acid, it yields hexahydrophthalic acid.

These acids show in their reactions, as well as in their constitution, great resemblance to succinic acid and its oxy-acids:—

Hexahydrophthalic Acid.

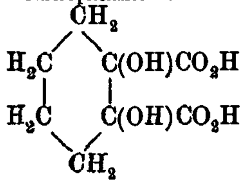


Succinic Acid.

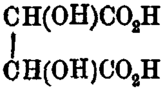


$$\begin{matrix}CH_2.CO_2H\\ |\\ CH_2.CO_2H\end{matrix}$$

Tartrophthalic Acid.

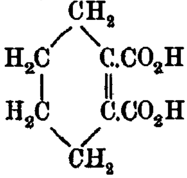


Tartaric Acid.

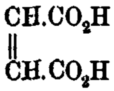


$$\begin{matrix}CH(OH)CO_2H\\ |\\ CH(OH)CO_2H\end{matrix}$$

Tetrahydrophthalic Acid.



Maleic Acid.



$$\begin{matrix}CH.CO_2H\\ \|\\ CH.CO_2H\end{matrix}$$

On heating hydromellitic acid or isohydromellitic acid with concentrated sulphuric acid, two isomerides of pyromellitic acid are formed together with trimesitic acid (page 389):—

$$(1)\ C_6H_6(CO_2H)_6 + 3SO_4H_2 = C_6H_2(CO_2H)_4 + 2CO_2 + 3SO_3 + 6H_2O$$

$$(2)\ C_6H_2(CO_2H)_6 + 3SO_4H_2 = C_6H_3(CO_2H)_3 + 3CO_2 + 3SO_2 + 6H_2O$$

Prehnitic Acid $C_6H_2(CO_2H)_4 + 2H_2O$ crystallizes from water in large prisms, resembling the mineral Prehnite. On heating, it loses water, and melts above 237° with the formation of the anhydride $C_6H_2(CO_2H)_2\left\{\begin{matrix}CO\\CO\end{matrix}\right\rangle O$. Nascent hydrogen converts it into *hydroprehnitic acid*, which yields isophthalic acid by heating it with sulphuric acid.

Mellophanic Acid $C_6H_2(CO_2H)_4$ is readily soluble in water, and forms crystalline crusts. Its barium salt is much more soluble than that of prehnitic acid.

Trimellitic Acid $C_6H_3(CO_2H)_3$.—By heating the hydropyromellitic acids with sulphuric acid, they are decomposed into pyromellitic anhydride, isophthalic acid, and trimellitic acid, crystallizing from water in warty masses, melting at 216°. The same acid has also been obtained, together with isophthalic acid, by oxidizing colophony with nitric acid.

Hemimellitic Acid $C_6H_3(CO_2H)_3$.—This isomeride of trimellitic acid and trimesitic acid is produced, together with phthalic acid, by heating hydromellophanic acid with sulphuric acid. It crystallizes in colourless needles, melting at 185°, and being resolved into carbon dioxide, water, phthalic anhydride, and benzoic acid.

Mellitic acid is, as we have seen, benzo-hexacarbonic acid; by taking out one molecule of carbon dioxide after the other, all other benzo-carbonic acids have been obtained, with the exception of the pentacarbonic acid. These acids may be arranged as follows:—

	Mellitic Acid. 1. 2. 3. 4. 5. 6.	
Pyromellitic Acid. 1. 2. 4. 5.	Prehnitic Acid. 1. 2. 3. 5.	Mellophanic Acid. 1. 2. 3. 4.
Trimellitic Acid. 1. 2. 4.	Trimesitic Acid. 1. 3. 5.	Hemimellitic Acid. 1. 2. 3.
Terephthalic Acid. 1. 4.	Isophthalic Acid. 1. 3.	Phthalic Acid. 1.2.
	Benzoic Acid. 1.	

ANILINE-COLOURS.

Aniline, toluidine, and pseudotoluidine are largely employed in the manufacture of a series of brilliant colours, which are used for dyeing wool and silk, and in calico-printing.

Mauveine $C_{27}H_{24}N_4$.—*Aniline-purple*, or *mauve*, consists of the sulphate of this base; it is obtained by mixing cold dilute solutions of potassium dichromate and aniline sulphate, and leaving the mixture to stand for some hours. A black precipitate is formed, containing only a few per cent. of mauve, which is extracted by alcohol. The same black precipitate is produced by boiling aniline sulphate with a solution of cupric chloride, and keeping the solution neutral by adding caustic soda. The reaction by which mauveine is formed is not understood, as the bye-products have not been analysed.

The blue colour which is produced by the action of bleaching-powder on aniline has been called *Runge's blue;* it consists of the salt of a base which is not mauveine, but is changed into it by boiling the solution.

Pure mauveine is obtained by adding caustic potash to a solution of the sulphate, the base separating out as a crystalline, almost black powder, which is almost insoluble in water, and dissolves in alcohol with a bluish-purple colour. It is a powerful base, decomposing ammonium salts, and absorbing readily carbon dioxide; its crystalline salts exhibit a golden metallic lustre, and dissolve in water, and more freely in alcohol, with a beautiful purple colour.

Mauveine Hydrochloride $C_{27}H_{24}N_4.ClH$ crystallizes in small prisms, and forms crystalline double salts with the chlorides of gold and platinum.

When mauve is heated with aniline, ammonia is given off, and a blue colouring matter is formed, the composition of which is not known.

By oxidizing a hot solution of mauve with sulphuric acid and manganese dioxide, a beautiful red colouring-matter is produced, which is very soluble in water, and forms small crystals having a fine beetle-green lustre. In concentrated sulphuric acid it dissolves with a dark-green colour, which, on adding gradually water in small quantities, changes into bluish-green, pure blue, violet, purple, and at last into pure red. To this beautiful substance the name "safranine" was originally given, but the colour occurring now in commerce under that name appears to be a different body.

Safranine $C_{21}H_{20}N_4$.—This base is a derivative of pseudotoluidine, and obtained by treating high-boiling commercial aniline with nitrous acid and oxidizing agents. The free base is readily soluble in water, and forms reddish-brown crystals, which, when heated to 100°, assume a faint beetle-green lustre.

Safranine Hydrochloride $C_{21}H_{20}N_4.ClH$ occurs in the forms of a paste in commerce, and is largely used in dyeing silk, as a substitute for safflower. It is very soluble in water, and precipitated from this solution by adding salt; it has been obtained by evaporation in fine reddish crystals. The nitrate is but sparingly soluble, and crystallizes in reddish-brown needles. The picrate is insoluble in water, and forms brown needles.

Safranine gives with sulphuric acid and water the same reactions as mauve-safranine.

Azodiphenyl-blue $C_{18}H_{15}N_3$ is obtained by heating amido-azobenzene with aniline hydrochloride and alcohol to 160°:—

$$N_2\left\{\begin{matrix} C_6H_5 \\ C_6H_4.NH_2 \end{matrix}\right. + C_6H_5.NH_2 = N_2\left\{\begin{matrix} C_6H_5 \\ C_6H_4.N(C_6H_5)H \end{matrix}\right. + NH_3$$

The free base is a dark-brown powder, which is insoluble in water. The hydrochloride is a dark-blue, indistinctly crystalline body, dissolving in alcohol with a deep bluish-violet colour.

ROSANILINE $C_{20}H_{19}N_3$.

The salts of this base are known by the names, *Aniline-red*, *Magenta*, or *Fuchsine*, and manufactured in considerable quantity by heating a mixture of aniline, toluidine, and pseudotoluidine (so-called magenta-aniline) with arsenic acid or other oxidizing agents:—

$$C_6H_7N + 2C_7H_9N + 3O = C_{20}H_{19}N_3 + 3H_2O$$

A hard mass is thus obtained, possessing the lustre of bronze, and containing arsenite and arsenate of rosaniline. It is purified by exhausting the melt with boiling water, and precipitating the solution with soda; the precipitate is, after washing, dissolved in an acid, and the solution evaporated to crystallization.

Rosaniline is also obtained by heating magenta-aniline with nitrobenzene:—

$$2C_7H_9N + C_6H_5.NO_2 = C_{20}H_{19}N_3 + 2H_2O$$

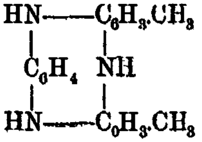
To obtain the pure base, ammonia is added to a hot aqueous solution of the acetate; the deep-red solution becomes almost colourless, and on cooling deposits the base in small white plates, having the composition $C_{20}H_{19}N_3.H_2O$. It is very sparingly soluble in water, and assumes a reddish tint when exposed to the air Rosaniline neutralizes acids, and forms a series of beautiful salts, exhibiting a fine beetle-green lustre, and dissolving in water, and more freely in alcohol, with a splendid red colour.

Rosaniline Hydrochloride $C_{20}H_{10}N_3.ClH$ crystallizes from a hot concentrated solution in rhombic prisms. It dissolves in hot hydrochloric acid with a yellowish-brown colour; and on cooling the acid salt $C_{20}H_{19}N_3(ClH)_3$ crystallizes out in brown needles, which, by water, are decomposed into hydrochloric acid and the monohydrochloride.

Both compounds form crystalline double salts with platinic chloride.

Rosaniline Acetate $C_{20}H_{10}N_3.C_2H_4O_2$ is readily soluble in water, and can easily be obtained in large splendid crystals.

The constitution of rosaniline is not known; but as it contains three atoms of hydrogen, which can be replaced by alcohol-radicals, it is probably constituted as follows:—



$$\begin{array}{lcl} HN & — & C_6H_3.CH_3 \\ | & & | \\ C_6H_4 & & NH \\ | & & | \\ HN & — & C_6H_3.CH_3 \end{array}$$

It is hardly doubtful that at least two rosanilines exist, one being derived from toluidine, and the other from pseudotoluidine.

Methyl-rosanilines.—By heating rosaniline or its acetate with methyl iodide and methyl-alcohol, hydrogen is replaced by methyl, and violet colours are produced, the shade of which is the bluer the more methyl groups are introduced. *Trimethyl-rosaniline* combines with methyl iodide, forming *rosaniline-tetramethylammonium iodide* $C_{20}H_{16}N_3(CH_3)_4I$; the corresponding hydrochloride is obtained on the large scale by heating dimethylaniline with potassium chlorate and cupric sulphate:—

$$3C_8H_{11}N + 3O = C_{24}H_{29}N_3O + 2H_2O$$

The free base is a reddish-brown powder, dissolving in alcohol with a violet colour. Its salts, as well as those of trimethyl-rosaniline and triethyl-rosaniline, possess in the dry state a golden-yellow lustre, and are found in commerce under the name of "Aniline-violets" and "Hofmann's violet."

In the process of manufacturing these violets, by the action of methyl or ethyl iodide on rosaniline, there is always produced a quantity of a dark resinous body, which is called "Hofmann gum." This bye-product yields by dry distillation a large quantity of methylaniline or ethylaniline.

Aniline-green is obtained by heating rosaniline with methyl alcohol and an excess of methyl iodide. The product is exhausted with boiling water, which leaves the greater part of the violet behind. To the solution salt is added to remove all the violet, and then it is neutralized with soda, and precipitated by picric acid. The salts of aniline-green contain the ammonium-base $C_{20}H_{16}(CH_3)_3N_3(CH_3O)_2$, which has not been much examined. The commercial product is a green paste, consisting of the picrate $C_{20}H_{16}(CH_3)_3N_3(CH_3.OC_6H_2(NO_2)_3)_2$, which in the pure state forms yellowish-green prisms, showing a copper-red reflection.

Phenyl-rosanilines.—When a rosaniline-salt is heated with aniline, hydrogen is replaced by phenyl, and ammonia is given off.

The salts of *monophenyl-rosaniline* $C_{20}H_{18}(C_6H_5)N_3$ have a reddish-violet colour, and those of *diphenyl-rosaniline* $C_{20}H_{17}(C_6H_5)_2N_3$ are bluish-violet. The salts of *triphenyl-rosaniline* $C_{20}H_{16}(C_6H_5)_3N_3$ have a pure blue colour, and are known by the name of "night-blue."

The formation of these blues takes place more readily in presence of acetic, benzoic, or other organic acids.

When triphenyl-rosaniline is submitted to dry distillation, it yields a considerable quantity of diphenylamine.

Triphenyl-rosanilinesulphonic Acid $C_{20}H_{16}(C_6H_5)_2(C_6H_4.SO_3H)N_3$ is obtained by dissolving triphenyl-rosaniline in concentrated sulphuric acid, and adding water to the solution, as a dark-blue mass, which dries up to grains having a beautiful metallic lustre. Its sodium salt is found in commerce under the name of "Nicholson's blue," or "alkali-blue;" it is a dark-grey, amorphous mass, dissolving in water, with a fine blue colour.

By the further action of sulphuric acid, other sulphonic acids are formed, which occur as sodium salts in several "soluble aniline blues."

Benzyl-rosaniline.—When a mixture of rosaniline, benzyl chloride, methyl iodide, and methyl alcohol is heated in a water-bath, the compound $C_{20}H_{16}(C_6H_5.CH_2)_3N_3.CH_3I$ is formed, crystallizing in beetle-green needles. The salts of this ammonium-base dye on silk a rich reddish-violet shade.

Leucaniline $C_{20}H_{21}N_3$.—The salts of this base are formed by treating rosaniline-salts with reducing agents. They are colourless, and readily oxidized to rosaniline-salts.

Chrysaniline $C_{20}H_{17}N_3$ is obtained as a bye-product in the manufacture of rosaniline. It is a yellow amorphous powder, and forms two series of yellow crystalline salts, containing either one or two equivalents of an acid.

Xylidine-red $C_{22}H_{23}N_3$.—Neither xylidine alone nor mixed with toluidine yields a colour, but when a mixture of aniline and xylidine is heated with arsenic acid, a red compound is produced, having the greatest resemblance to rosaniline.

PHENOL-COLOURS.

When phenols are heated with polybasic organic acids, either alone or in presence of sulphuric acid or glycerin, water is eliminated, and a series of peculiar compounds is formed, some being neutral bodies, while others dissolve in alkalis, forming intensely-coloured solutions, which are decolourized by reducing agents.

Some of the coloured bodies yield, when heated with sulphuric acid, new colours, which are also readily reduced in an alkaline solution, but not decolourized. The number of these compounds seems to be unlimited, but only a few have been more minutely studied.

Aurin $C_{20}H_{14}O_3$.—This compound is found in commerce under the name of "corallin," or "rosolic acid,"[1] and is used for dyeing silk and wool. It is prepared by heating phenol with oxalic acid and sulphuric acid. The commercial product is a brittle, resinous body, having a beetle-green lustre, and yielding a red powder. It is a mixture of different bodies; to obtain pure aurin from it, an alcoholic solution of ammonia is added to a cold concentrated alcoholic solution of the crude substance. A crystalline precipitate, a compound of aurin with ammonia, separates out, whilst the other bodies remain in solution. The ammonia-compound is washed with cold alcohol, and boiled with dilute acetic acid.

Aurin is but sparingly soluble in water, and crystallizes from alcohol in dull-red needles with a green lustre, and from acetic acid in rhombic prisms, having either the colour of chromic trioxide and a brilliant diamond lustre, or of a darker shade, showing a blue or green reflection. It dissolves readily in alkalis, with a magenta-red colour, and forms also with other oxides a series of very unstable salts.

---

[1] The name rosolic acid was first given to a red body existing in coal-tar, and was afterwards employed to designate all red compounds which may be obtained from phenol by different reactions.

Pure aurin is also readily obtained by heating *pure* phenol with oxalic acid and sulphuric acid for several days to 100°—110°. The product is boiled with water, dissolved in caustic soda, and precipitated with an acid. The crystalline precipitate is then crystallized from alcohol.

Aurin is also obtained by using formic acid in the place of oxalic acid, and its formation may therefore be expressed by the equation:—

$$3C_6H_6O + 2CO = C_{20}H_{14}O_3 + 2H_2O$$

When sulphur dioxide is passed into a hot concentrated alcoholic solution of aurin, the compound $(C_{20}H_{14}O_3)_2SO_2 + 5H_2O$ is formed, separating on cooling in brick-red crusts, or garnet-red granular crystals.

Aurin-potassium Sulphite $C_{20}H_{14}O_3 + KHSO_3$ is obtained by adding a solution of acid potassium sulphite to a hot alcoholic solution of aurin. It is a crystalline white powder, resembling precipitated chalk. The sodium and ammonium-compounds are similar bodies; they are easily decomposed by acids and alkalis.

Leucaurin $C_{20}H_{16}O_3$ is formed by heating an aqueous alkaline or acid alcoholic solution of aurin with zinc-dust. It crystallizes in thick colourless prisms or needles. It contains three hydroxyls, yielding with acetyl chloride *tri-acetyl-leucaurin* $C_{20}H_{13}O_3(C_2H_3O)_3$, crystallizing from alcohol in white silky needles.

Phenol-phthalein $C_{20}H_{14}O_4$ is produced by heating phenol with phthalic anhydride and sulphuric acid to 120°.

$$2C_6H_6O + C_8H_4O_3 = C_{20}H_{14}O_4 + H_2O$$

It is a colourless body, dissolving in caustic potash with a splendid red colour, which disappears on heating it with zinc-dust. Hydrochloric acid precipitates from the colourless solution *phenol-phthalin* $C_{20}H_{16}O_4$ in white granular crystals.

Fluorescein, or *Resorcin-phthalein* $C_{20}H_{12}O_5$, is formed by heating resorcin with phthalic anhydride. It forms small dark-brown crystals, dissolving in ammonia with a red colour; this solution exhibits, even when very diluted, a most beautiful green fluorescence. Zinc-dust reduces it to colourless *fluorescin*, and by heating it with sulphuric acid it is converted into a red compound, dissolving in alkalis with a blue colour, which, on adding zinc-dust, changes into red.

Hydroquinone-phthalein $C_{20}H_{12}O_5$ is obtained by heating hydroquinone with phthalic anhydride and sulphuric acid; it forms white crystals, melting at 232°, and dissolving in alkalis with a violet colour.

Gallein $C_{20}H_{12}O_7$ has been produced by heating pyrogallol with phthalic anhydride. It forms granular crystals, appearing brownish-red by reflected light, and blue by transmitted light. It dissolves in alcohol with a dark-red, and in alkalis with a beautiful blue colour, which soon becomes grey. On mordanted cloth, it dyes shades resembling those produced by brazil-wood. Reducing agents convert it into colourless *gallin* $C_{20}H_{18}O_7$.

Coerulein $C_{20}H_{10}O_7$ is obtained by heating gallin with sulphuric acid to 200°. It dissolves in aniline with a beautiful blue colour, and in alkalis with a blue colour; alum precipitates from this solution a green lake. By reduction it yields yellowish-red *coerulin*.

By using mellitic or pyromellitic acid in place of phthalic acid, compounds resembling the different phthaleins have been obtained. The constitution of the phenol-colours is not exactly known; but their constituents may be divided into two groups—the phenols, and the bodies which keep them together; the former being the chromogenous constituents, as the colour is but little changed by using different acids. A great number of natural colours, and chiefly those contained in the different dye-woods, have undoubtedly a similar constitution. The nature of the chromogenous constituents of these colours can in most cases be found by fusing the compound with caustic potash, or by treating it with nitric acid; but it will be far more difficult to detect the compounds which connect the chromogenous constituents, as in the natural colours this part seems to be played by compounds belonging to the sugar-group, or by vegetable acids which are not connected with the aromatic group.

The following compounds appear to be natural phenol-colours:—

Hæmatoxylin $C_{16}H_{14}O_6 + 3H_2O$ exists in logwood (*Hæmatoxylon Campechianum*), and crystallizes from water in yellow prisms, possessing a sweet taste, and turning the plane of polarization to the right. By fusing it with caustic potash it yields pyrogallol.

It dissolves with a red colour in ammonia, and this solution absorbs readily oxygen, *hæmatein* $C_{16}H_{12}O_6 + H_2O$ being formed, which is also produced by dissolving hæmatoxylin in ether, and adding fuming nitric acid. It forms brownish-red crystals, which lose water at 130°, and assume a green lustre. Hæmatin is slightly soluble in cold, and freely in boiling water; alkalis dissolve it with a beautiful deep-purple colour, and reducing agents reconvert it into hæmatoxylin.

Brasilin $C_{22}H_{20}O_7$ is found in brazil-wood, sapan-wood, peach-wood, &c. It crystallizes in large yellow prisms, dissolving in ammonia with a crimson, and in potash or soda with a purple colour. When nitric acid is added to its ethereal solution, crystalline *brasilein* is formed, and boiling nitric acid converts it into styphnic acid (page 343).

Carthamin $C_{14}H_{16}O_7$ is the colouring matter of safflower (the petals of *Carthamus tinctorius*). It is obtained by exhausting safflower with cold water, which dissolves a yellow colouring-matter; the residue is treated with a dilute solution of sodium carbonate, and the solution precipitated with acetic acid. Carthamin separates out as a flocculent precipitate, drying up to a beetle-green mass. It dissolves in alcohol with a splendid red colour, and forms with alkalis a yellowish-red solution. By fusing it with potash, it yields oxalic acid and para-oxybenzoic acid.

Bixin $C_{15}H_{18}O_4$ is the colouring-matter of "anotto" (from the fruit of *Bixa Orellana*). It is insoluble in water, and dissolves in alcohol and alkalis with a deep-yellow colour. When sulphur dioxide is passed into its alcoholic solution it becomes colourless.

Santalin $C_{15}H_{14}O_5$ is found in santal-wood, and forms microscopic bright red crystals, which are insoluble in water, but dissolve in alcohol with a red, and in alkalis with a violet colour. On adding barium chloride to its alkaline solution, a violet precipitate $(C_{15}H_{18}O_5)_2Ba$ is formed.

Euxanthic Acid $C_{10}H_{10}O_{10}$.—The magnesium salt of this acid is the chief constituent of *Indian yellow*, or *Purree*, a body of unknown origin, which is imported from India and China, and used in the painting of water-colours. By treating it with hydrochloric acid, euxanthic acid is obtained in yellow, silky needles, which have a sweetish bitter taste. On heating, it is resolved into water, carbon dioxide, *euxanthone*, and other products.

Euxanthone $C_{13}H_{18}O_4$ is a yellow, crystalline precipitate, and is also formed by the action of concentrated sulphuric acid on euxanthic acid. On fusing it with potash it is converted into *euxanthonic acid* $C_{13}H_{10}O(OH)_4$, crystallizing from water in long yellow needles. On heating it is resolved into water and euxanthone. Euxanthonic acid gives with ferric acid a red colour, while euxanthone is coloured green by this reagent.

Concentrated nitric acid forms with euxanthone nitro-products, which by prolonged action are converted into styphnic acid or trinitroresorcin.

When resorcin is heated with oxalic acid and sulphuric acid, a yellow substance is formed, containing apparently euxanthone.

Gentianin $C_{14}H_{10}O_5$ occurs in the root of *Gentiana lutea*, and crystallizes in pale-yellow needles, which are tasteless, and almost insoluble in water. It is soluble in water, and dissolves in alkalis with a deep-yellow colour, forming crystalline salts.

COMPOUNDS CONTAINING TWO OR MORE AROMATIC NUCLEI, LINKED TOGETHER BY CARBON.

DIPHENYL $C_{12}H_{10}$

Is obtained by the action of sodium on bromobenzene, and by passing the vapour of benzene through a red-hot tube :—

$$\begin{array}{c} C_6H_6 \\ \\ C_6H_6 \end{array} = \begin{array}{c} C_6H_5 \\ | \\ C_6H_5 \end{array} + H_2$$

It has also been produced by heating a mixture of potassium phenate and benzoate:—

$$C_6H_5.OK + C_6H_5.CO_2K = C_6H_5.C_6H_5 + CO_3K_2$$

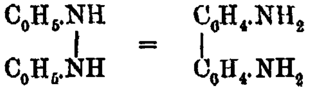
Diphenyl crystallizes from boiling alcohol in large, brilliant, thin plates, melting at 70°·5. It boils at 240°, and possesses a peculiar, aromatic smell. By heating it with a solution of chromic trioxide in glacial acetic acid, it is oxidized to benzoic acid.

Monobromodiphenyl $C_{12}H_9Br$ is obtained by adding bromine to a solution of diphenyl in carbon disulphide. It forms thin, large plates, melting at 89°, and boiling at 310°. Oxidizing agents convert it into parabromobenzoic acid.

Dibromodiphenyl $C_{12}H_8Br_2$ is formed by acting with bromine on diphenyl in the presence of water. It crystallizes from benzene in large colourless prisms, melting at 164°, and volatilizing at a high temperature. On oxidation it yields also parabromobenzoic acid.

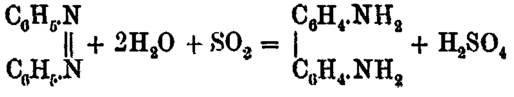
Dinitrodiphenyl $C_{12}H_8(NO_2)_2$.—When diphenyl is dissolved in cold concentrated nitric acid, two isomeric compounds are formed. One crystallizes in slender, colourless needles, melting at 213°; and the other, called *isodinitrodiphenyl*, which is more soluble in alcohol, forms large colourless crystals, melting at 93°·5.

Diamidophenyl, or *Benzidine*, $C_{12}H_8(NH_2)_2$, is not only produced by reducing the first of the dinitro-compounds with ammonium sulphide or tin and hydrochloric acid, but also by the action of acids on hydrazobenzene (page 328), the following molecular change taking place:—



$$\begin{array}{l} C_6H_5.NH \\ \quad | \\ C_6H_5.NH \end{array} = \begin{array}{l} C_6H_4.NH_2 \\ | \\ C_6H_4.NH_2 \end{array}$$

It is therefore conveniently prepared by passing sulphur dioxide into an alcoholic solution of azobenzene:—



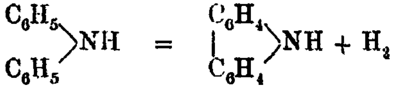
$$\begin{array}{l} C_6H_5.N \\ \quad \| \\ C_6H_5.N \end{array} + 2H_2O + SO_2 = \begin{array}{l} C_6H_4.NH_2 \\ | \\ C_6H_4.NH_2 \end{array} + H_2SO_4$$

Benzidine has also been obtained by acting with sodium on bromaniline.

It forms silvery scales, melting at 118°, and subliming, when more strongly heated, with partial decomposition.

Benzidine Sulphate $C_{12}H_8(NH_2)_2$ is a white powder, which is almost insoluble in water and alcohol.

Imidodiphenyl, or *Carbazol* $C_{12}H_8.NH$.—This body was first found in crude anthracene; it is produced synthetically by passing phenylaniline through a red-hot tube:—



$$\begin{array}{l} C_6H_5 \\ C_6H_5 \end{array}\!\!>NH = \begin{array}{l} C_6H_4 \\ | \\ C_6H_4 \end{array}\!\!>NH + H_2$$

Carbazol crystallizes from alcohol in white plates, melting at 238°, and boiling at 354°. Cold nitric acid colours it green in the cold, and on heating nitro-compounds are formed. It has no basic properties, but combines with picric acid like the aromatic hydrocarbons, forming the compound $C_{12}H_9N + C_6H_2(NO_2)_3OH$, which crystallizes from coal-tar naphtha in large red prisms.

Acetylcarbazol $C_{12}H_8N(C_2H_3O)$ is obtained by heating carbazol with acetic anhydride; it crystallizes from alcohol in flat prisms, melting at 69°, and combines with picric acid.

Carbazoline $C_{12}H_{13}.NH_2$.—This additive compound is formed by heating carbazol with hydriodic acid and phosphorus to 240°. It is a weak base, crystallizing from alcohol in tufts of silky needles, melting at 99°, and boiling at 296°. By heating its hydrochloride to 300° it loses hydrochloric acid and hydrogen, being converted into *hydrocarbazol* $C_{12}H_{13}N$, crystallizing from alcohol in warty masses possessing an unpleasant smell. It has no basic properties, but combines with picric acid.

Acridine $C_{12}H_9N$.—This isomeride of carbazol has also been found in crude anthracene. It crystallizes from dilute alcohol in transparent rhombic prisms, which have generally a yellowish-brown colour. It melts at 107°, and boils above 360°, but sublimes even at as low a temperature as 100° in large, broad needles. It has basic properties, and forms well-defined salts, which, as well as the free base, produce a burning pain on the skin, and attack violently the mucous membranes, the least quantity giving rise to violent sneezing.

Diphenylene Oxide $C_{12}H_8O$ is produced by distilling triphenyl phosphate with quicklime; it forms small plates, melting at 80°, boiling at 273°, and possessing an agreeable odour. It is not changed by passing it over red-hot zinc-dust, nor by heating it with hydriodic acid to 250°.

Diphenylmonosulphonic Acid $C_{12}H_9.SO_3H$ is obtained by heating equal molecules of diphenyl and sulphuric acid until water and the hydrocarbon begin to volatilize. The potassium salt $C_{12}H_9.SO_3K$ crystallizes from hot water in very slender long needles, which after some time change into a heavy powder. The barium- and calcium-salts are precipitates, which can be crystallized from boiling water.

Diphenyldisulphonic Acid $C_{12}H_8(SO_3H)_2$ is produced by heating the hydrocarbon with an excess of sulphuric acid. The potassium salt $C_{12}H_8(SO_3K)_2 + 5H_2O$ forms long thick prisms. The barium- and lead-salts are insoluble in water. By decomposing the latter with hydrogen sulphide in the presence of water, the free acid is obtained, which on evaporation is left in deliquescent prisms, melting at 72°·5, and decomposing above 200°.

Dioxydiphenyl $C_{12}H_8(OH)_2$.—This phenol is prepared by acting with nitric trioxide on benzidine nitrate, and boiling the diazo-compound with water:—

$$C_{12}H_8\left\{\begin{matrix}N{=}N{-}NO_3\\ N{=}N{-}NO_3\end{matrix}\right. + 2H_2O = C_{12}H_8\left\{\begin{matrix}OH\\ OH\end{matrix}\right. + 2N_2 + 2HNO_3$$

It resembles common phenol, crystallizing in needles, which dissolve sparingly in water, but freely in alcohol.

Hexoxydiphenyl $C_{12}H_4(OH)_6$.—The tetramethyl-ether of this phenol is formed by the dry distillation of beech- and birch-wood, and therefore occurs in crude wood-vinegar, which is purified by the addition of potassium dichromate. Blue films are deposited, consisting of the corresponding quinone, or *caerolignone* $C_{12}H_4(OCH_3)_4O''_2$, which is obtained pure by dissolving the precipitate in cold phenol, from which it is precipitated by alcohol in dark steel-blue needles. It is insoluble in all ordinary solvents, and neither distils nor sublimes without decomposition. Reducing agents reconvert it into *tetramethyl-hexoxydiphenyl*, or *hydrocaerolignone* $C_{12}H_4(OCH_3)_4(OH)_2$, crystallizing from alcohol in colourless monoclinic prisms, melting at 190°, and distilling, when carefully heated, without decomposition. By adding sodium ethylate to its alcoholic solution, the phenate $C_{12}H_4(OCH_3)_4(ONa)_2$ is obtained as a yellow, neutral precipitate.

When hydrocaerolignone is heated with hydrochloric acid to 200°, it is resolved into methyl chloride and *hexoxydiphenyl*, crystallizing from boiling water in beautiful plates, grouped in rosettes, and dissolving in alkalis with a splendid purple colour. Red-hot zinc-dust reduces it to diphenyl.

DIPHENYL-METHANE, OR BENZYL-BENZENE $CH_2\left\{\begin{matrix}C_6H_5\\ C_6H_5\end{matrix}\right.$.

This hydrocarbon was first obtained by distilling diphenylacetic acid $(C_6H_5)_2CH.CO_2H$ with baryta. It is also produced by heating benzyl chloride with benzene and zinc-dust to 150°. When the action is once started, the zinc may be withdrawn, without hindering the completion of the reaction, during which currents of hydrochloric acid are evolved:—

$$C_6H_5.CH_2Cl + C_6H_6 = C_6H_5.CH_2.C_6H_5 + HCl$$

Besides benzyl-benzene, other products are formed, of which two isomeric hydrocarbons $C_{20}H_{18}$ have been isolated. We cannot, as yet, explain why such a stable body as benzene takes part in this reaction with such great energy.

Diphenyl-methane crystallizes in monoclinic prisms, melting at 26°·5, and possessing the odour of oranges.

Benzyl-phenol, or *Benzyl-oxybenzene*, $C_6H_5.CH_2.C_6H_4.OH$ has been obtained by heating benzyl chloride with phenol and zinc-dust. It crystallizes from alcohol in lustrous plates, melting at 84°, and dissolves in caustic alkalis, but not in ammonia.

Benzylphenyl-methyl Ether, or *Benzyl-anisol* $C_6H_5.CH_2.C_6H_4.OCH_3$, is formed by the action of zinc on a mixture of anisol (page 332) and benzyl chloride. It is a limpid, mobile liquid, possessing an aromatic odour, and boiling at about 305°. On heating it with hydriodic acid to 170°, it is resolved into benzyl-phenol and methyl iodide.

Diphenyl Ketone, or *Benzophenone*.—The ketone of benzoic acid has been produced by different reactions:—

(1.) By the dry distillation of calcium benzoate:—

$$\left.\begin{matrix} C_6H_5.CO.O \\ C_6H_5.CO.O \end{matrix}\right\} Ca = \left.\begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix}\right\} CO + CO \left\{\begin{matrix} O \\ O \end{matrix}\right\} Ca$$

(2.) By heating mercury-diphenyl with benzoyl chloride in closed tubes:—

$$(C_6H_5)_2Hg + 2C_6H_5.COCl = 2C_6H_5.CO.C_6H_5 + HgCl_2$$

(3.) By heating a mixture of benzene, benzoic acid, and phosphorus pentoxide to 200°:—

$$C_6H_6 + C_6H_5.CO.OH = C_6H_5.CO.C_6H_5 + H_2O$$

Benzophenone crystallizes from alcohol in rhombic prisms, melting at 49°, and boiling at 300°. An isomeric modification is obtained by oxidizing diphenyl-methane with chromic acid solution. It forms transparent monoclinic crystals, melting at 26°. After some time they become opaque, and change into the common rhombic modification.

Monochlorobenzophenone $C_6H_4Cl.CO.C_6H_5$ has been prepared by heating monochlorobenzene with benzoic acid and phosphorus pentoxide. It crystallizes from a mixture of ether and alcohol in tufts of brilliant flat needles, melting at 76°.

Diphenyl Carbinol, or *Benzhydrol* $(C_6H_5)_2CH.OH$.—This secondary alcohol is produced by the action of nascent hydrogen on benzophenone; it crystallizes in silky needles, melting at 67°·5.

PHENYL-TOLYL-METHANE, OR BENZYL-TOLUENE $CH_2\left\{\begin{matrix} C_6H_5 \\ C_6H_4.CH_3 \end{matrix}\right.$

Is one of the products obtained by heating a mixture of toluene and benzyl chloride with zinc-dust. It is a liquid boiling at 277°, and possessing a fragrant, fruity smell.

Tolyl-phenol Ketone $CO\left\{\begin{matrix} C_6H_5 \\ C_6H_4.CH_3 \end{matrix}\right.$ exists in two modifications, which have been obtained by oxidizing benzyl-toluene, and by heating a mixture of toluene, benzoic acid, and phosphorus pentoxide to 200°. One crystallizes in flat pointed plates, melting at 57°. On heating it with soda-lime to 270°, it is resolved into benzene and paratoluic acid. The other modification is a liquid.

Benzoyl-benzoic Acid $C_6H_5.CO.C_6H_4.CO_2H$ is produced by oxidizing benzyl-toluene or tolyl-phenyl ketone with potassium dichromate and dilute sulphuric acid. It crystallizes in thin needles or plates, melting at 194°, and sublimes at a high temperature in brilliant needles.

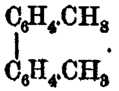
Benzhydryl-benzoic Acid $C_6H_5.CH(OH).C_6H_4.CO_2H$.—This glycollic acid is a product of the action of tin and hydrochloric acid on an alcoholic solution of benzoyl-benzoic acid. It is more freely soluble in water than the latter, and crystallizes in needles, melting at 165°; it cannot be sublimed, but decomposes when more strongly heated.

Benzyl-benzoic Acid $C_6H_5.CH_2.C_6H_4.CO_2H$.—To obtain this compound, benzhydryl-benzoic acid is heated with concentrated hydriodic acid. This reaction is perfectly analogous to the formation of acetic acid from glycollic acid. It crystallizes from alcohol in glistening needles, melting at 155°, and subliming without decomposition. When heated with lime it is resolved into carbon dioxide and diphenylmethane.

BENZYL-ETHYL-BENZENE $C_6H_5.CH_2.C_6H_4.C_2H_5$

Is formed by heating a mixture of benzyl chloride and ethyl-benzene with zinc. It is a liquid having a faint aromatic smell, and boiling at 294°. On oxidation, it yields benzoyl-benzoic acid.

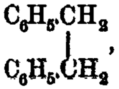
DITOLYL



$$\begin{array}{l} C_6H_4.CH_3 \\ | \\ C_6H_4.CH_3 \end{array}.$$

To prepare this hydrocarbon, solid bromotoluene is treated with sodium. It crystallizes from ether in splendid monoclinic prisms, melting at 121°. An isomeride has been obtained by the action of sodium on monochlorotoluene; it is a liquid boiling at 272°.

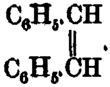
DIBENZYL, OR DIPHENYL-ETHANE



$$\begin{array}{l} C_6H_5.CH_2 \\ \qquad | \\ C_6H_5.CH_2 \end{array},$$

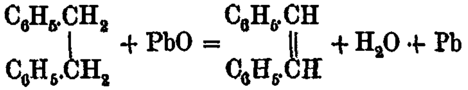
Is produced by acting with sodium on benzyl chloride. It crystallizes from ether in large monoclinic prisms, melting at 52°, and boiling at 284°.

STILBENE, TOLUYLENE, OR DIPHENYL-ETHENE



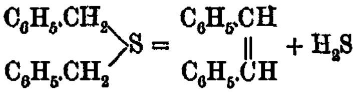
$$\begin{array}{l} C_6H_5.CH \\ \qquad \| \\ C_6H_5.CH \end{array}.$$

This hydrocarbon is formed by the action of sodium on benzaldehyde or benzylene dichloride, as well as by passing the vapour of benzyl-chloride over heated soda-lime, or the vapour of dibenzyl over hot lead oxide:—



$$\begin{array}{c} C_6H_5.CH_2 \\ | \\ C_6H_5.CH_2 \end{array} + PbO = \begin{array}{c} C_6H_5.CH \\ \| \\ C_6H_5.CH \end{array} + H_2O + Pb$$

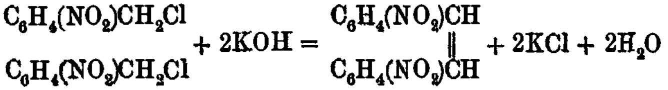
It is, however, most conveniently prepared by submitting benzyl sulphide to dry distillation:—



$$\begin{array}{l} C_6H_5.CH_2 \diagdown \\ \qquad\qquad\quad >S \\ C_6H_5.CH_2 \diagup \end{array} = \begin{array}{c} C_6H_5.CH \\ \| \\ C_6H_5.CH \end{array} + H_2S$$

On slow evaporation of its ethereal solution, it is obtained in large monoclinic plates, melting at 120°, and boiling at 306°. By heating it with concentrated hydriodic acid it is reduced to dibenzyl.

Dinitrostilbene $C_{14}H_{10}(NO_2)_2$ has been produced synthetically by heating nitrobenzyl chloride with alcoholic potash:—

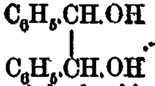


$$\begin{array}{c} C_6H_4(NO_2)CH_2Cl \\ \\ C_6H_4(NO_2)CH_2Cl \end{array} + 2KOH = \begin{array}{c} C_6H_4(NO_2)CH \\ \| \\ C_6H_4(NO_2)CH \end{array} + 2KCl + 2H_2O$$

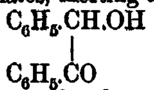
It forms brilliant yellow needles, having a green lustre, and sublimes in yellow plates. By heating it with alcoholic ammonium sulphide in sealed tubes to 100°, it is converted into *diamidostilbene* $C_{14}H_{10}(NH_2)_2$, crystallizing from alcohol in white plates, melting at 170°. The hydrochloride $C_{14}H_{10}(NH_3)_2Cl_2$ forms white plates.

Toluylene or *Stilbene Dibromide* $C_{14}H_{12}Br_2$, separates out in needles when bromine is added to a solution of stilbene in ether. By heating it with alcoholic potash it is converted into *monobromostilbene* $C_{14}H_{11}Br$, an oily liquid, distilling with partial decomposition.

Toluylene Glycol $C_{14}H_{12}(OH)_2$ exists in several isomeric modifications. Two of them are obtained by heating stilbene dibromide with silver acetate and glacial acetic acid, and boiling the product with alcoholic potash. One crystallizes in rhombic prisms, melting above 115°; and the other, called *isotoluylene glycol*, forms slender needles, melting at 96°.



Hydrobenzoin $\begin{array}{c} C_6H_5.CH.OH \\ | \\ C_6H_5.CH.OH \end{array}$.—This third isomeride is formed by the action of zinc and hydrochloric on benzaldehyde. It forms large rhombic plates, melting at 130°.

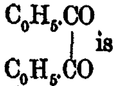


Benzoin $\begin{array}{c} C_6H_5.CH.OH \\ | \\ C_6H_5.CO \end{array}$ is produced by heating hydrobenzoin, or the two toluylene glycols, gently with nitric acid, and was first obtained by adding benzaldehyde to an alcoholic solution of potassium cyanide. It is therefore also formed by the action of alcoholic potash on crude oil of bitter almonds. It forms colourless prisms, melting at 137°. Acetyl chloride converts it into the *monacetate* $C_{14}H_{11}O_2.C_2H_3O$, and nascent hydrogen into hydrobenzoin.

Stilbene Glycol.—This fourth isomeric glycol is formed together, with other products, when benzoin is heated with alcoholic potash. It crystallizes in four-sided flat prisms, melting at 132°. Acetyl chloride converts it into the *diacetate* $C_{14}H_{12}(OC_2H_3O)_2$, forming colourless needles melting at 135°.

Deoxybenzoin, or *Phenyl-benzyl Ketone* $\left.\begin{matrix}C_6H_5\\C_6H_5.CH_2\end{matrix}\right\}CO$, was first obtained by the action of zinc, and hydrochloric acid on benzoin. It is also readily produced by heating monobromostilbene with water to 180°, and, together with other products, by distilling a mixture of benzoate and phenylacetate of calcium. It crystallizes from alcohol in plates, melting at 55°.

Stilbyl Alcohol, or *Phenyl-benzyl Carbinol* $\left.\begin{matrix}C_6H_5\\C_6H_5.CH_2\end{matrix}\right\}CH.OH$, is produced by the action of sodium-amalgam on a hot alcoholic solution of deoxybenzoin. It forms glistening, slender needles, melting at 62°. Nitric acid oxidizes it to deoxybenzoin, and by boiling with dilute sulphuric acid it is resolved into water and stilbene. Acetyl chloride converts it into *stilbyl acetate*, a colourless, oily liquid.

Benzil, or *Dibenzoyl*  $\begin{matrix}C_6H_5.CO\\|\\C_6H_5.CO\end{matrix}$ is obtained by the action of nitric acid or chlorine on benzoin, or by treating deoxybenzoin with bromine, and heating the bromide $C_6H_5CBr_2.CO.C_6H_5$, thus formed with water. Benzil crystallizes from alcohol in large, hexagonal prisms, melting at 90°. Nascent hydrogen re-converts it into benzoin.

Benzilic Acid, or *Diphenylglycollic Acid* $(C_6H_5)_2C(OH)CO_2H$ is formed when benzil is heated with a little potash and alcohol to 100°. It is readily soluble in alcohol and hot water, and crystallizes in small monoclinic needles, melting at 150°, and possessing a bitter taste. Oxidizing agents resolve it into water, carbon dioxide, and diphenyl ketone, and when its barium salt is heated with a little soda-lime, it splits up into carbon dioxide and diphenyl ketone.

These reactions show that this acid contains the two phenyl-groups linked to one carbon-atom, and therefore in its formation from benzil a molecular change must have taken place.

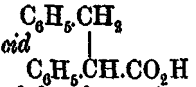
Diphenylacetic Acid $(C_6H_5)_2CH.CO_2H$ is produced by the action of concentrated hydriodic acid on benzilic acid. It crystallizes from boiling water in needles, melting at 146°. When heated with baryta it is resolved into carbon dioxide and diphenyl-methane.

Diphenyltrichlorethane $(C_6H_5)_2CH.CCl_3$ is obtained by the action of sulphuric acid on a mixture of benzene and chloral:—

$$2C_6H_6 + COH.CCl_3 = (C_6H_5)_2CH.CCl_3 + H_2O$$

It crystallizes from alcohol in shining white plates, melting at 64°. On heating with alcoholic potash it is converted into *Diphenyldichlorethene* $(C_6H_5)_2C.CCl_2$ crystallizing in large flat prisms, melting at 80°.

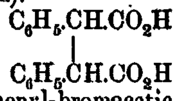
Diphenylpropionic Acid, or *Dibenzylcarbonic Acid*



$$\begin{array}{l} C_6H_5.CH_2 \\ \quad | \\ C_6H_5.CH.CO_2H \end{array}$$

The ethyl-ether of this acid has been obtained by the action of sodium-amalgam on a mixture of benzyl chloride and ethyl chlorocarbonate. Diphenylpropionic acid crystallizes from alcohol in thin needles, melting at 84°. On heating with lime it is resolved into carbon dioxide and dibenzyl (or stilbene and hydrogen).

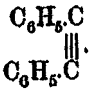
Diphenylsuccinic Acid, or *Dibenzyldicarbonic Acid*



$$\begin{array}{l} C_6H_5.CH.CO_2H \\ \quad | \\ C_6H_5.CH.CO_2H \end{array}$$

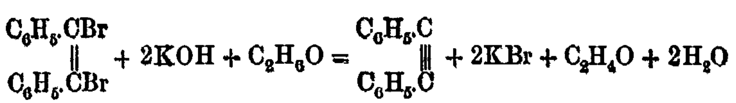
is produced by the action of alcoholic potash on phenyl-bromacetic acid, $C_6H_5.CHBr.CO_2H$. It forms hard white prisms, and when heated with lime yields dibenzyl and stilbene.

TOLANE, OR DIPHENYL-ETHINE



$$\begin{array}{l} C_6H_5.C \\ \quad ||| \\ C_6H_5.C \end{array}.$$

To prepare this body, stilbene dibromide must be heated with alcoholic potash for a long time. It forms long prismatic crystals, melting at 60°. With bromine it forms *tolane dibromide* $C_{14}H_{10}Br_2$, which exists in two isomeric modifications; one crystallizing in white, flat scales, melting at 200°, and the other in long, brittle needles, melting at 64°. When either of them is heated with water to 180°, for some hours, a large portion is always converted into the other modification. On heating them with alcoholic potash, tolane is regenerated, and aldehyde is formed, which by the potash is converted into aldehyde-resin:—



$$\begin{array}{l} C_6H_5.CBr \\ \quad || \\ C_6H_5.CBr \end{array} + 2KOH + C_2H_6O = \begin{array}{l} C_6H_5.C \\ \quad ||| \\ C_6H_5.C \end{array} + 2KBr + C_2H_4O + 2H_2O$$

This example shows very well the energetic resistance which hydrogen, contained in the aromatic nucleus, offers to oxidation. Thus while stilbene dibromide, when acted on by alcoholic potash, readily loses the two hydrogen-atoms contained in the side-chain in the form of water, tolane dibromide under the same conditions parts only with the bromine, and the oxygen of the potash converts the alcohol into aldehyde.

DIMESITYL-METHANE $CH_2\begin{cases}C_6H_2(CH_3)_3\\C_6H_2(CH_3)_3\end{cases}$

This compound is readily obtained by the action of sulphuric acid on a solution of mesitylene, and formaldehyde, or methyl alcohol and chromic trioxide in glacial acetic acid :—

$$2C_6H_3(CH_3)_3 + CH_2O = CH_2[C_6H_2(CH_3)_3]_2 + H_2O$$

It crystallizes from ether in large monoclinic prisms, melting at 130°.

TRIPHENYL-METHANE $CH(C_6H_5)_3$.

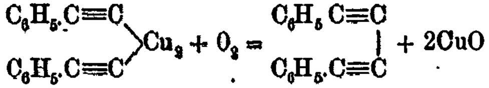
To prepare this hydrocarbon, mercury-diphenyl is heated with benzylene dichloride to 150°.

$$C_6H_5.CHCl_2 + 2(C_6H_5)_2Hg = CH(C_6H_5)_3 + 2C_6H_5HgCl$$

On evaporating its alcoholic solution, it separates out in large lustrous crystals, melting at 92°·5. It combines with benzene, forming large transparent crystals, consisting of $CH(C_6H_5)_3 + C_6H_6$, and melting at 76°. When this compound is exposed to the air, benzene volatilizes, and the crystals become opaque and brittle. Triphenylmethane does not combine with toluene.

DIPHENYL-DIETHINE $C_4(C_6H_5)_2$.

When copper-ethinyl-benzene (page 385) is shaken with concentrated alcoholic ammonia in presence of air, the following reaction takes place :—



$$\left.\begin{array}{l}C_6H_5.C\equiv C\\C_6H_5.C\equiv C\end{array}\right>Cu_2 + O_2 = \begin{array}{c}C_6H_5.C\equiv C\\|\\C_6H_5.C\equiv C\end{array} + 2CuO$$

Diphenyl-diethine crystallizes from alcohol in long needles, melting at 94°, it combines with bromine, forming a viscid octobromide $C_4Br_8(C_6H_5)_2$.

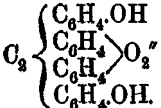
DIPHTHALYL $C_6H_4<\begin{matrix}CO-CO\\CO-CO\end{matrix}>C_6H_4$

When phthalic acid is boiled with phosphorus pentachloride, it is converted into *phthalyl chloride* $C_6H_4(COCl)_2$, which, when heated with silver-dust, yields *diphthalyl*, a crystalline solid, melting a little above 300°, and subliming in soft, pale-yellow, interlaced needles. Nitric acid oxidizes it to *diphthalic acid* $(C_6H_4)_2(CO)_2(CO.OH)_2$, forming microscopic needles, melting at 265°. By heating this acid above its melting-point, it yields diphthalyl, and phthalic anhydride, whilst by boiling it with nitric acid for some time it is oxidized to phthalic acid.

TETRAPHENYL-ETHENE $C_2(C_6H_5)_4$.

By acting with phosphorus pentachloride on diphenyl ketone it is converted into *diphenyl-dichloromethane* $(C_6H_5)_2CCl_2$, and this compound, when heated with silver-dust, yields tetraphenyl-ethene, crystallizing from hot benzene in pointed prisms, melting at 221°. Hot concentrated sulphuric acid converts it into *tetraphenyl-tetrasulphonic acid*, which, when fused with potash, yields the corresponding phenol, or

Tetroxytetraphenyl-ethene $C_2(C_6H_4.OH)_4$ crystallizing from hot glacial acetic acid in very thin, small plates, which in the air assume a faint violet tinge. On adding ferric chloride to a solution of this phenol in acetic acid, a dark blood-red liquid is formed, from which crystals, having a metallic lustre, and consisting of



$$C_2\left\{\begin{matrix}C_6H_4.OH\\ \left.\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}\right\rangle O_2''\\ C_6H_4.OH.\end{matrix}\right.$$

separate out on standing. This quinone is insoluble in water, and dissolves sparingly in alcohol, but freely in alkalis, with an intensely bluish-green colour, which, by the action of zinc-dust, disappears. These properties show that this compound is nearly related to the phenol-colours.

Benzpinacone, or *Tetraphenyl-ethene Glycol* $(C_6H_5)_4C_2(OH)_2$ is produced by the action of zinc and sulphuric acid on diphenyl ketone:—

$$\begin{matrix}(C_6H_5)_2CO\\ \\ (C_6H_5)_2CO\end{matrix} + H_2 = \begin{matrix}(C_6H_5)_2C.OH\\ |\\ (C_6H_5)_2C.OH\end{matrix}$$

It forms very small prisms, melting at about 180°; oxidizing agents convert it again into diphenyl ketone, and with water and sodium amalgam it yields diphenyl carbinol.

DIPHENYL-BENZENE $C_6H_4(C_6H_5)_2$.

This hydrocarbon is formed, together with diphenyl, when benzene is passed through a red-hot tube, and is also produced, by the action of sodium on a mixture of monobromobenzene and paradibromobenzene. It forms colourless crystals melting at 205°, and boiling at about 400°. On oxidizing it with a solution of chromic trioxide in glacial acetic acid it yields *paradiphenylcarbonic* or *paraphenylbenzoic acid* $C_6H_5.C_6H_4.CO_2H$, crystallizing from alcohol in tufts of needles, melting at 216°, and subliming in long needle-shaped crystals. By heating it with lime it is resolved into carbon dioxide and diphenyl, and by further oxidation it is converted into terephthalic acid.

TRIPHENYL-BENZENE $C_6H_3(C_6H_5)_3$

Is formed by heating methyl-phenyl ketone with phosphorus pentoxide; this reaction is perfectly analogous to the formation of mesitylene from dimethyl ketone:—

$$3C_6H_5.CO.CH_3 = (C_6H_5)_3C_6H_3 + 3H_2O$$

It crystallizes from ether in short prisms, melting at 167°.

INDIGO-GROUP.

Indigotin, or *Indigo-blue* $C_{16}H_{10}N_2O_2$, occurs as glucoside, called *Indican*, $C_{52}H_{62}N_2O_{34}$ in different species of *Indigofera*, growing in India, Africa, and South America, and in *Isatis tinctoria*, *Polygonum tinctorium* and *Nerium tinctorium*. It is a brown syrup, having a nauseous, and bitter taste. On boiling it with a dilute mineral acid, it is resolved into a kind of sugar and indigotin:—

$$C_{52}H_{62}N_2O_{34} + 4H_2O = C_{16}H_{10}N_2O_2 + 6C_6H_{10}O_6$$

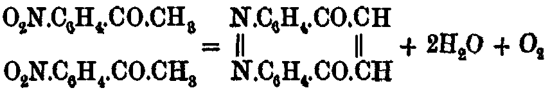
Indigo is obtained by macerating the plants with water, exposing the liquid in flat vessels to the air, and stirring it up frequently. Fermentation soon sets in, and indigo is deposited as a blue powder, It comes into the market in the form of cubic cakes, which, when rubbed with a hard body, exhibit a copper-red lustre.

Indican sometimes occurs in human urine which, on standing or by adding an acid, deposits indigotin.

Commercial indigo is a mixture of different bodies; to obtain pure indigotin, finely powdered indigo, grape-sugar, and strong soda-lye, are put in a flask, which is filled with hot alcohol and corked. In the place of grape-sugar and alcohol, ferrous sulphate, and hot water may be used. After standing for some hours, a yellow, clear solution is obtained, containing hydro-indigotin or indigo-white; on exposing it to the air it absorbs oxygen, and indigotin is precipitated as a crystalline powder.

Indigotin has a deep-blue colour with a purple tinge; it is insoluble in water, alcohol, dilute acids, and alkalis, but dissolves in boiling aniline, with a fine blue colour, and in hot paraffin with a purple colour; on cooling it is deposited in crystals. When heated to about 300°, it volatilizes in purple vapours, condensing in prisms, having a purple lustre.

Indigotin has also been obtained synthetically by heating the syrupy modification of methyl-nitrophenyl ketone until it is converted into a solid mass, which, when carefully heated with soda-lime and zinc-dust, yields a small quantity of indigotin. This reaction gives a clue to the constitution of indigotin:—



$$\begin{array}{l} O_2N.C_6H_4.CO.CH_3 \\ O_2N.C_6H_4.CO.CH_3 \end{array} = \begin{array}{l} N.C_6H_4.CO.CH \\ \| \qquad\qquad\quad \| \\ N.C_6H_4.CO.CH \end{array} + 2H_2O + O_2$$

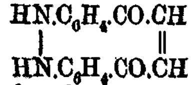
When indigo is boiled with caustic soda and manganese dioxide it yields 1·2 amidobenzoic acid:—

$$2(N.C_6H_4.CO.CH) + 6NaOH + 2O_2 = \\ 2(H_2N.C_6H_4.CO_2Na) + 2Na_2CO_3 + 2H_2O$$

By distilling indigo with potash, pure aniline is obtained:—

$$2(N.C_6H_4.CO.CH) + 8KOH + 2H_2O = \\ 2(H_2N.C_6H_5) + 4K_2CO_3 + 4H_2$$

Hydro-indigotin, or *Indigo-white* $C_{16}H_{12}N_2O_2$ =



$$\begin{array}{l} HN.C_6H_4.CO.CH \\ \ \ | \qquad\qquad\quad \| \\ HN.C_6H_4.CO.CH \end{array}$$

stands in the same relation to indigotin as hydrazobenzene to azobenzene. To obtain the pure compound, its alkaline solution, which has been mentioned already under indigotin, is decomposed by hydrochloric acid in an atmosphere of carbon dioxide; the precipitate is washed with water, which has been freed from air by boiling, and dried in a current of hydrogen.

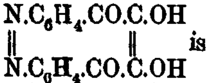
Indigo-white is a crystalline white powder, which in the moist state rapidly absorbs oxygen, and is oxidized to indigotin.

The existence of this compound is made use of in the dyeing of cotton-goods. An "indigo-vat" is prepared by mixing one part of powdered indigo with two parts of ferrous sulphate, three parts of slaked lime, and 200 parts of water. After the mixture has stood for some time, the goods are steeped in the liquid and then exposed to the air, when indigotin is gradually deposited in the fibre.

Indigotinsulphonic Acids.—Indigo or indigotin dissolves in highly concentrated sulphuric acid with a deep-blue colour; on diluting this solution with water, a blue precipitate of the *monosulphonic acid*, or *sulphopurpuric acid* $C_{16}H_9N_2O_2.SO_3H$, is obtained, which is insoluble in dilute acids, but dissolves in water. Its purple salts dissolve in water with a blue colour.

The filtrate from this acid contains *indigotindisulphonic acid* (indigo-sulphuric acid) $C_{16}H_8N_2O_2(SO_3H)_2$, which is separated from the excess of sulphuric acid, by steeping white wool into the liquid until it is dyed a deep blue. After being washed with water, the wool is treated with ammonium carbonate, and the blue solution precipitated with lead acetate. On decomposing the precipitate with hydrogen sulphide, a colourless solution of hydro-indigotindisulphonic acid is obtained, which readily absorbs oxygen and leaves on evaporation indigotindisulphonic acid as a blue amorphous mass. It forms blue amorphous salts.

Potassium and *Sodium indigotindisulphonates* are obtained as blue precipitates by neutralizing a solution of indigo in sulphuric acid with potassium or sodium carbonate. They are insoluble in salt-solutions, but dissolve in water with a fine blue colour and are found in commerce under the name of "indigo-carmine," or "indigo-extract."

Isatin $C_{16}H_{10}N_2O_4$ = 

$$\begin{array}{l} N.C_6H_4.CO.C.OH \\ \| \qquad\qquad\quad \| \\ N.C_6H_4.CO.C.OH \end{array}$$

is conveniently prepared by adding gradually nitric acid to a boiling mixture of finely-powdered indigo and water, until the blue colour has completely disappeared. It crystallizes from hot water in brilliant yellowish-red prisms, dissolving in water and alcohol with a brown colour, and yielding with alkalis a violet solution. When alcoholic potash is carefully added to an alcoholic solution of isatin and silver nitrate, a wine-red precipitate of *silver isatite* $C_{16}H_8Ag_2N_2O_4$ is obtained.

On heating isatin it melts, and sublimes with partial decomposition. It combines with the acid sulphites of the alkali-metals, forming crystalline compounds.

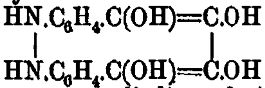
When heated with a solution of phosphorus in phosphorus trichloride, it gives a green solution, from which, after adding water and exposing the liquid to the air, indigotin is gradually deposited, which is formed by the reducing action of the phosphorus.

Nitrous acid converts it into nitrosalicylic acid, and on distilling it with potash it yields aniline, hydrogen and potassium carbonate. By passing chlorine into its hot aqueous solution, it is converted into *dichlorisatin* $C_{16}H_8Cl_2N_2O_4$, crystallizing in orange-red prisms, and *tetrachlorisatin* $C_{16}H_6Cl_4N_2O_4$, which forms reddish needles. When these two compounds are distilled with potash, they yield monochlor- and dichloraniline, which compounds were discovered by this reaction. Bromine acts on it in an analogous manner.

Isatindisulphonic Acid $C_{16}H_8N_2O_4(SO_3H)_2$ has been obtained by oxidizing indigotindisulphonic acid with chromic acid. It is very soluble in water, and does not crystallize well. Its salts have a red or orange colour. *Barium isatindisulphonate* $C_{10}H_8N_2O_4(SO_3)_2Ba$ crystallizes in bright-red scales.

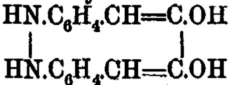
Trioxindol or *Isatic Acid* $C_{10}H_{14}N_2O_6$.—When the violet solution of isatin in potash is heated, it becomes yellow, and, on evaporation, yellow crystals of *potassium isatate* $C_{16}H_{12}K_2N_2O_6$ are deposited. By decomposing it with an acid, trioxindol is obtained as a white powder, which is soluble in water, and is resolved by heat into isatin and water.

Hydro-isatin or *Isatyde* $C_{16}H_{12}N_2O_4$.—This hydrazo-compound is formed by the action of hydrochloric acid and zinc, or ammonium sulphide on isatin. It is not soluble in water, but dissolves in alcohol, and forms thin, colourless crystals.



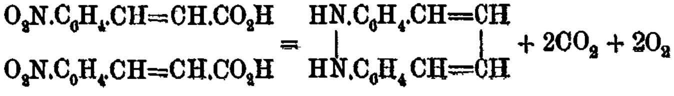
Dioxindol $C_{16}H_{14}N_2O_4$ = $\begin{array}{l} HN.C_6H_4.C(OH){=}C.OH \\ \vert \qquad\qquad\qquad\quad \vert \\ HN.C_6H_4.C(OH){=}C.OH \end{array}$ is produced by the action of sodium-amalgam on an alkaline solution of isatin. On evaporation the sodium salt $C_{16}H_{12}Na_2N_2O_4 + 4H_2O$ is obtained in silvery crystals.

Dioxindol crystallizes in yellow prisms; it is soluble in water and alcohol, and combines not only with bases but forms also with acids crystalline compounds. When heated it melts, and then decomposes, aniline being formed. The oxygen of the air oxidizes it to isatin, and on heating it with silver oxide it yields benzaldehyde.



Oxindol $C_{16}H_{14}N_2O_2$ = $\begin{array}{l} HN.C_6H_4.CH{=}C.OH \\ \vert \qquad\qquad\quad \vert \\ HN.C_6H_4.CH{=}C.OH \end{array}$ is formed by treating dioxindol with hydrochloric acid and tin or sodium-amalgam. It crystallizes from hot water in colourless needles, melting at 120°. It volatilizes without decomposition, and when its aqueous solution is exposed to the air it absorbs oxygen, and is oxidized to dioxindol and isatin. It combines with bases and with acids.

Indol $C_{10}H_{14}N_2$ has boen obtained by heating oxindol with zinc-dust, and synthetically by fusing metanitrocinnamic acid with caustic potash and iron-filings:—



$$\begin{array}{l} O_2N.C_6H_4.CH{=}CH.CO_2H \\ \\ O_2N.C_6H_4.CH{=}CH.CO_2H \end{array} = \begin{array}{l} HN.C_6H_4.CH{=}CH \\ \vert \qquad\qquad\quad \vert \\ HN.C_6H_4\,CH{=}CH \end{array} + 2CO_2 + 2O_2$$

Indol is also one of the products of the pancreatic digestion, and the indican sometimes occuring in urine is derived from this source; this is shown by the fact that after the subcutaneous injection of indol, a considerable quantity of indican constantly appears in the urine.

Indol is a weak base crystallizing from hot water in large colourless plates. melting at 52°, and possessing a disagreeable odour, which it imparts to the fæces. It readily volatilizes with steam, and can be distilled without decomposition. When very dilute red fuming nitric acid is added to its aqueous solution, a red crystalline precipitate is formed, which by boiling with the water, is reconverted into indol. A different compound, crystallizing in long red needles, is obtained by passing nitrogen trioxide into its alcoholic solution. When pine-wood is steeped in an alcoholic solution of indol, containing hydrochloric acid, the wood assumes a cherry-red colour, which soon changes into a brownish-red.

NAPHTHALENE-GROUP.

NAPHTHALENE $C_{10}H_8$.

This hydrocarbon is formed by the destructive distillation of many carbon-compounds, a larger yield being obtained when the products are exposed to a red heat. It is, therefore, found in quantity in coal and wood-tar. But even substances which are comparatively rich in hydrogen as alcohol, ether, acetic acid, &c., yield some naphthalene, when their vapour is passed through a red-hot tube.

It occurs also in "Rangoon tar," or the petroleum from Burmah, and has been produced synthetically by passing the vapour of phenylbutene dibromide (page (402), through a red-hot tube:—

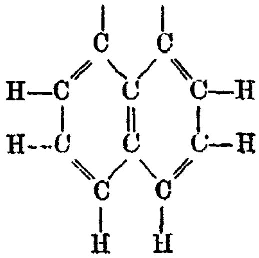
$$C_6H_5.C_4H_7Br_2 = C_6H_4.C_4H_4 + 2HBr + H_2$$

Naphthalene is obtained from the portion of coal-tar boiling between 180° to 220° from which, on cooling, crude naphthalene crystallizes out, which is purified by pressing it to remove oily substances, and then submitting it to sublimation or crystallization from alcohol.

Naphthalene crystallizes in large, transparent, brilliant plates, melting at 80°, and possessing a faint, peculiar odour and a burning taste. It boils at 217°, but sublimes readily at a much lower temperature. On mixing hot alcoholic solutions of naphthalene and picric acid, the compound $C_{10}H_8 + C_6H_2(NO_2)_3OH$ crystallizes on cooling in golden-yellow needles, which are grouped in stars. This compound is not decomposed by re-crystallization from alcohol or benzene, but ammonia resolves it into its constitutents.

When naphthalene is boiled with dilute nitric acid, it is oxidized to phthalic acid and oxalic acid.

In its chemical character, naphthalene bears a great resemblance to benzene, and its constitution is best explained by the following graphical formula:—



Naphthalene, therefore, would consist of two aromatic nuclei, which have two atoms of carbon in common. The correctness of this hypothesis has been proved in the following way:—

When naphthalene is oxidized, phthalic acid $C_6H_4(CO_2H)_2$ is formed; this acid can be obtained in two different ways from naphthalene; viz., either by destroying the one or the other aromatic nucleus. Such an experiment cannot, of course, be made with naphthalene itself, because we have no means of distinguishing between the two groups. It appears, therefore, necessary, first, to replace hydrogen in one of the nuclei, and then find out, which is attacked and which not.

On oxidizing dichloronaphthaquinone, $C_{10}H_4Cl_2O''_2$, phthalic acid is formed, a fact proving that in the quinone all the oxygen and chlorine are combined with those four atoms of carbon which are oxidized, the formula of dichloronaphthaquinone being, therefore, $C_6H_4.C_4Cl_2O''_2$. By acting with phosphorus pentachloride on this compound, the dyad group, O''_2, is replaced by chlorine, and at the same time one atom of hydrogen is substituted, pentachloronaphthalene being formed:—

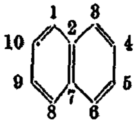
$$C_{10}H_4Cl_2O_2'' + 2PCl_5 = C_{10}H_3Cl_5 + HCl + 2POCl_3$$

Now, if by the oxidation of this compound the same carbon-atoms were attacked as in the quinone, monochlorophthalic acid would be formed, but the product was found to be tetrachlorophthalic acid, which proves that the second aromatic nucleus has now been destroyed, and that naphthalene has really the constitution assigned to it. This will be clearly seen by the following formulæ:—

Naphthalene.
$C_4H_4.C_2.C_4H_4$

Dichloronaphthaquinone.	Pentachloronaphthalene.
$C_4H_4.C_2.C_4Cl_2O_2''$	$C_4H_3Cl.C_2.C_4Cl_4$
Phthalic Acid.	Tetrachlorophthalic Acid.
$C_4H_4.C_2(CO_2H)_2$	$(CO_2H)_2C_2.C_4Cl_4$

Whilst among the mono-substituted benzenes no isomeric forms occur, we find that the monosubstitution-products of naphthalene can exist in two isomeric modifications. This can also be easily explained from the constitution of this hydrocarbon. By representing it by two hexagons and numbering the corners,



we find that each of the carbon-atoms occupying the positions 1, 3, 6, and 8, is combined with one other (2 or 7) in which all the combining units are saturated with carbon, whilst the atoms 4, 5, 9 and 10, are combined with carbon-atoms to which hydrogen is attached. The functions of the atoms 1, 3, 6 and 8 will, therefore, differ from those of the four latter.

Naphthalene forms additive compounds much more readily than benzene.

HYDRONAPHTHALENES.

Dihydronaphthalene, or *Naphthydrene* $C_{10}H_{10}$.—When naphthalene is heated with potassium a black compound is formed, having probably the composition $C_{10}H_8K_2$, inasmuch as water decomposes it into caustic potash and dihydronaphthalene. The same hydrocarbon is produced when naphthalene is heated with 20 parts of concentrated hydriodic acid to 280°. It is a colourless, oily liquid, boiling at 210° and possessing a penetrating smell.

Tetrahydronaphthalene $C_{10}H_{12}$ is obtained by heating 10 parts of naphthalene with 3 parts of amorphous phosphorus and 9 parts of hydriodic acid to 250°. It is a liquid, boiling at 205°, and possesses a peculiar, but not strong odour.

Both hydrides are resolved into naphthalene and hydrogen, when their vapour is passed through a red-hot tube.

NAPHTHALENE CHLORIDES.

Naphthalene Dichloride $C_{10}H_8Cl_2$.—When chlorine is passed over naphthalene, it melts and absorbs the chlorine completely, the first product being naphthalene dichloride, a heavy, pale-yellow oil, which by repeated distillation, or by the action of alcoholic potash, is resolved into hydrochloric acid, and monochloronaphthalene.

Naphthalene Tetrachloride $C_{10}H_8Cl_4$ is produced by the continued action of chlorine on the dichloride, and is a solid, crystallizing from chloroform in transparent rhombic plates, melting at 182°.

Dichloronaphthydrene Glycol $C_{10}H_8Cl_2(OH)_2$ is obtained by heating the tetrachloride with 30 parts of water to 190°. It is soluble in water, and crystallizes from ether in large, hard prisms. By heating it with acetyl chloride it is converted into the *diacetate* $C_{10}H_8Cl_2(OC_2H_3O)_2$, crystallizing from ether in hard, short prisms, melting at 130°.

Naphthalene Dichlorhydrate $C_{10}H_8\left\{\begin{matrix}Cl_2\\(OH)_2\end{matrix}\right.$ is obtained by dissolving naphthalene in concentrated hypochlorous acid, and forms pale-yellow prisms. Alcoholic potash converts it into *naphthene alcohol*, or *naphthalene tetrahydroxide* $C_{10}H_8(OH_4)$, crystallizing from alcohol in colourless prisms.

SUBSTITUTED NAPHTHALENES.

Monochloronaphthalene $C_{10}H_7Cl$ is conveniently prepared by boiling naphthalene dichloride with alcoholic potash. It is a thin, colourless, strongly refractive liquid, boiling at 251°, and smelling like naphthalene.

a Dichloronaphthalene $C_{10}H_6Cl_2$ is produced by the action of caustic potash on naphthalene tetrachloride. It is a crystalline mass, melting at 36°, and boiling at 281°.

β Dichloronaphthalene is obtained, together with its isomeride as a bye-product in the preparation of the tetrachloride, and crystallizes in glistening, brittle prisms, melting at 68°, and boiling at 282°.

The different chloronaphthalenes combine like naphthalene with chlorine, whilst the naphthalene chlorides yield products of substitution by the further action of chlorine. By decomposing these different additive products with alcoholic potash, higher chlorinated, naphthalenes are obtained, which are all crystalline solids, and exist in different isomeric forms.

Perchloronaphthalene $C_{10}Cl_8$ is the final product of this reaction, and forms brilliant rhombic crystals, melting at 135°, and boiling at 403°.

Monobromonaphthalene $C_{10}H_7Br$.—Bromine does not combine with naphthalene, but forms substitution-products, the first being monobromonaphthalene, a colourless liquid boiling at 277°.

Dibromonaphthalene $C_{10}H_6Br_2$, crystallizes in long silky needles, melting at 81°.

The higher brominated naphthalenes are also crystalline solids.

Moniodonaphthalene $C_{10}H_7I$ is formed by the action of iodine *on* mercury-dinaphthyl; it is a thick, colourless liquid, boiling above 300°.

Mononitronaphthalene $C_{10}H_7.NO_2$ is best prepared by dissolving naphthalene in glacial acetic acid, and boiling the solution with common nitric acid for half an hour. It crystallizes from alcohol in pale-yellow prisms, melting at 61°, and subliming when carefully heated.

a Dinitronaphthalene $C_{10}H_6(NO_2)_2$ is formed, together with the following compound, by boiling naphthalene with concentrated nitric acid until the oily layer has completely disappeared. It is sparingly soluble in glacial acetic acid, and forms colourless prisms, melting at 211°.

β Dinitronaphthalene is more freely soluble in acetic acid, and crystallizes in brilliant, yellow, rhombic plates, melting at 170°.

Both compounds are not volatile, but deflagrate on heating.

a Trinitronaphthalene $C_{10}H_5(NO_2)_3$ is formed by boiling, *a* dinitronaphthalene with red fuming nitric acid. It crystallizes from chloroform in large monoclinic plates, melting at 122°, and detonating when more strongly heated.

β Trinitronaphthalene is formed by adding concentrated sulphuric acid to a mixture of β dinitronaphthalene, and fuming nitric acid. It forms fine crystals, melting at 213°.

γ *Trinitronaphthalene* has been obtained by heating α dinitronaphthalene with a mixture of sulphuric and nitric acids. It crystallizes from nitric acid in brilliant, pale-yellow plates, melting at 147°.

α *Tetranitronaphthalene* $C_{10}H_4(NO_2)_4$ is produced by the continued action of nitric acid on the α nitro-compounds. It crystallizes from chloroform in light-yellow, hard, rhombic prisms, melting at 259°.

β *Tetranitronaphthalene* is obtained in the same way from the β compounds, and forms thin needles, melting at 200°.

Amidonaphthalene, or *Naphthylamine* $C_{10}H_7.NH_2$, is prepared from nitronaphthalene by the same reactions by which nitrobenzene is converted into aniline. It crystallizes in colourless needles, melting at 50°, and possessing a disagreeable odour like indol. It boils at 300°, and is almost insoluble in water, but dissolves freely in alcohol. Its salts crystallize well, and by acting with an oxidizing agent on their solution, a blue precipitate is formed, which soon changes into a purple powder of oxy-amidonaphthalene $C_{10}H_7O(NH_2)$.

Naphthyl-phenylamine, or Phenyl-amidonaphthalene $NH\left\{\begin{matrix}C_{10}H_7\\C_6H_5\end{matrix}\right.$, is formed by heating aniline and amidonaphthalene hydrochloride to 280° for 36 hours:—

$$C_{10}H_7.NH_2.ClH + C_6H_5\,NH_2 = NH_4Cl + NH\left\{\begin{matrix}C_{10}H_7\\C_6H_5\end{matrix}\right.$$

It forms small crystals, melting at 60°, and boiling at 315°; its solution exhibits dichroism.

α *Di-amidonaphthalene, or Naphthidine* $C_{10}H_6(NH_2)_2$, is obtained by the action of reducing agents on α dinitronaphthalene, and forms brilliant prisms, melting at 175°. Its sulphate and hydrochloride are but sparingly soluble in water.

β Dinitronaphthalene forms an isomeric compound.

Amidoazonaphthalene $N_2\left\{\begin{matrix}C_{10}H_7\\C_{10}H_6.NH_2\end{matrix}\right.$ is produced by adding potassium nitrite to a solution of amidonaphthalene hydrochloride. It crystallizes in orange needles, having a beetle-green lustre, and forms salts, having an intensely violet colour, but which are very unstable, being decomposed by water. On silk it dyes a fine orange shade, which on dipping it in hydrochloric acid becomes purple, and on washing with water again yellow.

Azodinaphthyl-red $N_2\left\{\begin{matrix}C_{10}H_7\\C_{10}H_6.NH(C_{10}H_7)\end{matrix}\right.$ is obtained by heating amidoazonaphthalene with amidonaphthalene. The free base is hardly known. The hydrochloride is used for dyeing silk, and found in commerce under the name "Magdala-red." It dissolves in alcohol with a-deep red colour, and crystallizes in needles, having a beetle-green lustre. Its dilute solution exhibits a splendid bright-red fluorescence. The salts of this base are not decomposed by alkalis, but only by long digestion with water and silver-oxide.

Naphthalenesulphonic Acid $C_{10}H_7.SO_3H$ exists in two isomeric forms, which are produced by dissolving naphthalene in hot, strong sulphuric acid. To separate them the dilute boiling solution is neutralized with lead carbonate; on cooling, the lead salt of the β acid crystallizes in thick scales, and by evaporating the mother-liquor the salt of the α acid is obtained in large thin plates. Both salts are purified by crystallization, and decomposed by hydrogen sulphide.

α Naphthalenesulphonic Acid is a crystalline, deliquescent mass, which, when heated with dilute hydrochloric acid to 200°, is resolved into naphthalene and sulphuric acid:—

$$C_{10}H_7.SO_3H + H_2O = C_{10}H_8 + SO_4H_2$$

β Naphthalenesulphonic Acid is a soft, laminated, crystalline mass, which is not deliquescent and hardly changed by hydrochloric acid at 200°. Its salts are less soluble in water than those of the α acid, and more stable at a high temperature.

OXYNAPHTHALENES.

Monoxynaphthalene, or Naphthol $C_{10}H_7.OH$.—The phenol of naphthalene exists in two isomeric modifications, which are obtained by fusing the sulphonic acids with potash.

α Naphthol crystallizes from hot water in silky monoclinic needles, melting at 94°, and boiling at 280°, but subliming at a much lower temperature. It has a burning taste and a faint smell, resembling that of common phenol. Its dust attacks the mucous membranes, and produces violent sneezing. By adding a solution of bleaching-powder or ferric chloride to its aqueous solution, it assumes a deep-violet colour, and soon a flocculent, violet precipitate makes its appearance.

β Naphthol forms small, brilliant needles, melting at 122°, boiling at 290°, and subliming when gently heated without previously melting. It has a burning taste, but hardly any smell; its dust produces sneezing. With bleaching-powder or ferric chloride it does not yield a violet colouration.

Both naphthols readily form metallic compounds, like other phenols.

α Naphthyl-ethyl Ether $\left.\begin{matrix}C_{10}H_7\\ C_2H_5\end{matrix}\right\}O$ is obtained by acting with ethyl iodide on an alcoholic solution of potassium α naphthate. It is a colourless liquid, boiling at 280°, and possessing a peculiar smell.

β Naphthyl-ethyl Ether is produced by the same reaction from β naphthol, and forms a crystalline mass, melting at 33°, and smelling like pine-apple.

Monochloronaphthol $C_{10}H_6Cl.OH$ has been obtained by distilling dichloronaphthydrene glycol with hydrochloric acid. It forms long, thin, and exceedingly fine needles, melting at 109°, and emitting the odour of phenol. On dissolving it at a gentle heat in a little sulphuric acid, and adding a crystal of oxalic acid, a violet colour is produced. The production of this phenol may be explained by assuming that a chlorhydrate is formed as an intermediate product, which readily loses hydrochloric acid, just as naphthalene tetrachloride yields by dry distillation dichloronaphthalene:—

$$C_{10}H_8Cl_2\left\{\begin{matrix}Cl\\OH\end{matrix}\right. = C_{10}H_6Cl.OH + 2HCl$$

Mononitronaphthol $C_{10}H_6(NO_2)OH$.—When amidonaphthalene is boiled with glacial acetic acid, it yields acetyl-amidonaphthalene, which by adding fuming nitric acid to its solution in acetic acid is converted into the mononitro-compound. By boiling this body with concentrated soda, it yields the sodium compound of mononitronaphthol:—

$$C_{10}H_6(NO_2)N\left\{\begin{matrix}H\\C_2H_3O\end{matrix}\right. + 2NaOH = C_{10}H_6(NO_2)OH + C_2H_3NaO_2 + NH_3$$

It crystallizes from boiling water in golden-yellow needles, melting at 164°, and forms salts having an orange or red colour. The same compound is formed, but only in a small quantity, by the continued action of potash-lime on nitronaphthalene in presence of air.

α Dinitronaphthol $C_{10}H_5(NO_2)_2OH$ is obtained on the large scale by adding sodium nitrite to a solution of amidonaphthalene and hydrochloric acid, and boiling the diazonaphthalene chloride thus formed with nitric acid. It is also produced by gently heating a solution of *α* naphtholsulphonic acid with nitric acid.

α Dinitronaphthol crystallizes from alcohol in lemon-yellow needles, melting at 138°, and has pronounced acid properties, decomposing carbonates, and forming salts having a yellow or orange colour. The sodium and calcium salts are used for dyeing wool yellow, and known by the name "naphthalin-yellow."

β Dinitronaphthol.—Pure *β* naphthol is not nitrated by nitric acid, but by heating its alcoholic solution with nitric acid the dinitro-compound is formed. It crystallizes in brilliant, pale-yellow needles, melting at 195°, and forms salts having a yellow or orange colour.

Dioxynaphthalene $C_{10}H_6(OH)_2$.—To prepare this body, naphthalene is heated for some time with sulphuric acid, in order to convert it into naphthalenedisulphonic acid, which is fused with potash. Dioxynaphthalene is sparingly soluble in water, and freely in alcohol, and crystallizes in needles, which sublime on heating. Its solution exhibits a bluish-green fluorescence.

Naphthoquinone $C_{10}H_6O_2$ is formed by treating a solution of naphthalene in warm glacial acetic acid, with a solution of chromic trioxide in the same solvent. It readily sublimes in bright-yellow crystals, melting at 125°, and is volatile in the vapour of water at 100°, communicating to it a pungent odour, resembling that of ordinary quinone.

Naphthohydroquinone $C_{10}H_6(OH)_2$ is prepared by boiling the quinone with strong hydriodic acid and amorphous phosphorus; on cooling, the hydroquinone is deposited in long colourless needles, melting at 176°. Oxidizing agents reconvert it into the quinone. It differs from the isomeric dioxynaphthalene by being more readily soluble in water.

Naphthoquinhydrone $C_{10}H_6 \cdot \left\{ \begin{array}{l} O.O.C_{10}H_6.OH \\ O.O.C_{10}H_6.OH \end{array} \right.$—This body is obtained by boiling an aqueous solution of napthohydroquinone with naphthoquinone, or by boiling the latter with weak hydriodic acid, and amorphous phosphorus; it forms dark-purple crystals.

Dichloronaphthoquinone $C_6H_4Cl_2O_2$ is produced by the action of potassium chlorate and hydrochloric acid on *a* dinitronaphthol. It crystallizes from hot alcohol in yellow needles.

Dichloronaphthohydroquinone $C_6H_4Cl_2(OH)_2$ is obtained by boiling the preceding compounds with hydriodic acid and phosphorus, and crystallizes in colourless prisms.

Oxychloronaphthoquinone, or *Chloroxynaphthalic Acid* $C_{10}H_4(OH)ClO_2$, is formed by treating chloronaphthalene dichloride with nitric acid; it forms yellow crystals, melting above 200°, and forms salts having a yellow or red colour. By dissolving dichloronaphthoquinone in hot soda-solution a crimson liquid is obtained, containing the sodium-salt:—

$$C_{10}H_4Cl_2O_2 + 2NaOH = C_{10}H_4(ONa)ClO_2 + NaCl + H_2O$$

Dioxynaphthoquinone, or *Naphthazarin* $C_{10}H_4(OH)_2O_2$.—This compound is prepared by heating sulphuric acid to 200°, and adding one-tenth of its weight of *a* dinitronaphthalene, and then gradually zinc. After cooling the solution is diluted with 10 parts of water, boiled and filtered. The gelatinous mass which separates out on cooling is crystallized from alcohol, and thus the compound is obtained in brown needles having a green lustre. On heating it sublimes in feathery tufts with a brilliant beetle-green reflection. In alkalis it dissolves with a beautiful blue colour; this solution yields blue precipitates with the salts of barium, calcium, and lead; alum produces a red lake and ferric salts a bluish-grey precipitate. Red-hot zinc-dust reduces it to naphthalene, and when sodium-amalgam is added to its aqueous solution it becomes colourless, showing that this body is a quinone, whilst its metallic compounds prove that it is also a phenol.

Naphthylpurpuric Acid $C_{11}H_7N_3O_4$.—By acting with potassium cyanide on an alcoholic solution of *a* dinitronaphthol a deep-red solution containing the potassium salt of this acid is obtained. The free acid has not yet been obtained, but a series of salts has been prepared, resembling the isopurpurates, but crystallizing not so well (see page 336). On fusing them with potash, they yield hemimellitic acid $C_6H_3(CO_2H)_3$.

Indophane $C_{22}H_{10}N_4O_4$ is produced together with naphthylpurpuric acid by adding a hot concentrated solution of potassium cyanide to a solution of *a* dinitronaphthol in ammonia. A violet precipitate, having a brilliant beetle-green lustre, is obtained, and purified by washing it with hydrochloric acid; this compound is only soluble in acetic acid and sulphuric acid, forming a beautifully coloured solution. The potassium salt $C_{22}H_9KN_4O_4$ is produced by heating indophane with solution of potash as a blue powder having a copper-red lustre.

MERCURY-DINAPHTHYL $Hg\begin{cases}C_{10}H_7\\C_{10}H_7\end{cases}$.

This compound is formed by boiling a solution of bromonaphthalene in benzene with sodium-amalgam. It crystallizes in colourless prisms, melting at 243°. Hydrochloric acid resolves it into mercuric chloride and naphthalene.

METHYL-NAPHTHALENE $C_{10}H_7.CH_3$.

This hydrocarbon is produced, but not readily, by action of sodium on a mixture of bromonaphthalene and methyl iodide. It is a limpid liquid boiling at 232°, and not solidifying even at $-$ 18°.

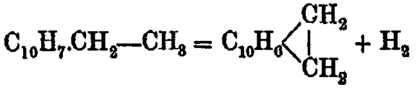
Ethyl-naphthalene $C_{10}H_7.C_2H_5$ is a similar liquid, boiling at 252°.

Menaphthylamine $C_{10}H_7.CH_2.NH_2$.—This powerful base is obtained by converting *a* cyanonaphthalene by means of hydrogen sulphide into *menaphthothiamide* $C_{10}H_7.CS.NH_2$, and treating an alcoholic solution of this compound with zinc and hydrochloric acid.

Menaphthylamine is a very caustic liquid, boiling at 290°; it readily absorbs carbon dioxide and forms, with acids, salts crystallizing very readily.

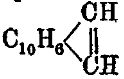
ACENAPHTHENE, OR ETHENE-NAPHTHALENE $C_{10}H_6.C_2H_4$.

This compound exists in coal-tar, and is deposited in crystals by leaving the portion boiling at 265° to 280°, to stand in a cold place. It crystallizes from hot alcohol in long needles, melting at 95°, and boiling at 268°. By boiling it with dilute sulphuric acid and potassium dichromate, it is oxidized to bibasic *naphthalic acid* $C_{10}H_6(CO_2H)_2$, which sublimes in long serrated plates, melting at 266°; by heating it for some time to 140° to 150°, it is converted into the anhydride $C_{10}H_6(CO)_2O$, and by distilling the calcium salt with slaked lime, pure naphthalene is obtained. Acenaphthene has also been produced synthetically by passing ethyl-naphthalene through a red-hot tube :—



$$C_{10}H_7.CH_2—CH_3 = C_{10}H_6\left\langle\begin{matrix}CH_2\\ |\\ CH_2\end{matrix}\right. + H_2$$

The two side-chains are probably linked to two adjoining carbon-atoms of the naphthalene-nucleus, because naphthalic acid has so great a resemblance to phthalic acid.



Ethine-naphthalene $C_{10}H_6\left\langle\begin{matrix}CH\\ \|\\ CH\end{matrix}\right.$ is obtained by passing the vapour of acenaphthene over heated lead oxide. It crystallizes from alcohol in large, lustrous, golden-yellow plates, melting at 93°. On oxidation it yields naphthalic acid.

NAPHTHONITRILES.

α *Napthonitrile* $C_{10}H_7.CN$ is formed by distilling a mixture of potassium cyanide and potassium, α naphthalenesulphonate. It has also been prepared by heating amidonaphthalene oxalate, whereby it is resolved into water, carbon dioxide, and *naphthyl-formamide* $C_{10}H_7N(COH)H$, which, when heated with concentrated hydrochloric acid, loses water, and is converted into the nitrile.

It crystallizes from petroleum-naphtha in broad silky needles, melting at 37°·5, and boiling at 298°.

β *Naphthonitrile* is obtained from β naphthalenesulphonic acid, and forms crystalline scales, melting at 66°·5, and boiling at 305°.

NAPHTHALENECARBONIC ACIDS.

By heating the nitriles with alcoholic potash the corresponding acids are formed.

α *Naphthoic Acid*, or *Naphthyl-formic Acid* $C_{10}H_7.CO_2H$, is sparingly soluble in boiling water, and freely in hot alcohol. It crystallizes in needles, melting at 160°.

β *Naphthoic Acid* crystallizes in needles, melting at 182°; its salts are less soluble than the α naphthoates. By distilling a mixture of calcium β naphthoate, and formate, some naphthalene is formed and β *naphthoic aldehyde*, crystallizing from boiling-water in thin glistening plates, melting at 59°·5.

Both acids are, when heated with baryta, resolved into carbon dioxide and naphthalene. A mixture of them is prepared on the large scale, and used in the place of benzoic acid in the manufacture of aniline-blue.

α Oxynaphthoic Acid $C_{10}H_6(OH)CO_2H$ is formed by action with sodium and carbon dioxide on α naphthol. It is sparingly soluble in water, and crystallizes in needles which are grouped in stars, and melt at 186°. Its solution is coloured pure-blue by ferric chloride.

β Oxynaphthoic Acid is not so readily formed; it crystallizes like the α acid, and gives with ferric chloride a blackish-violet colour.

Naphthalene-bicarbonic Acids $C_{10}H_6(CO_2H)_2$.—The nitriles of these acids, which are isomeric with naphthalic acid (page 437), are produced by distilling the potassium salts of the different modifications of naphthalene-bromosulphonic, and disulphonic acids with potassium cyanide. The nitrile from bromonaphthalenesulphonic acid yields a naphthalene-bicarbonic acid, which is almost insoluble in water, and crystallizes in microscopic needles, melting at 240°.

The other modifications have been but little studied.

NAPHTHYL-PHENYL-METHANE $CH_2\left\{\begin{matrix}C_6H_5.\\C_{10}H_7\end{matrix}\right.$

This hydrocarbon has been prepared by heating a mixture of benzyl chloride and naphthalene with zinc; it forms brilliant needles, melting at 64°.

α Naphthyl-phenyl Ketone $CO\left\{\begin{matrix}C_6H_5\\C_{10}H_7\end{matrix}\right.$ is produced by heating a mixture of benzene, α naphthoic acid, and phosphorus pentoxide. It crystallizes in short prisms, melting at 75°·5.

β Naphthyl-phenyl Ketone has been obtained by the same reaction from β naphthoic acid. It forms tufts of white needles, melting at 82°.

A mixture of these two ketones is also formed by heating naphthalene with benzoic acid and phosphorus pentoxide.

DINAPHTHYLS $C_{20}H_{14}$.

Dinaphthyl is obtained by the action of sodium on bromonaphthalene, and together with phthalic acid by oxidizing naphthalene with manganese dioxide and dilute sulphuric acid. It crystallizes in pearly scales, melting at 154°.

Isodinaphthyl.—This isomeride is produced together with hydrogen, by passing naphthalene repeatedly through a red-hot tube. It forms brilliant plates, melting at 200°, and boiling above 300°; its alcoholic solution exhibits a fine blue fluorescence.

α Dinaphthyl Ketone $CO\left\{\begin{matrix}C_{10}H_7\\C_{10}H_7\end{matrix}\right.$ is obtained by heating *α* naphthoic acid with naphthalene and phosphorus pentoxide. It crystallizes from boiling alcohol in pointed needles, and from a mixture of ether and alcohol in thick prisms, melting at 135°.

β Dinaphthyl Ketone forms small needles melting at 135°; it is much less soluble in alcohol than the *α* compound.

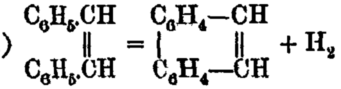
PHENANTHRENE-GROUP.

PHENANTHRENE $C_{14}H_{10}$

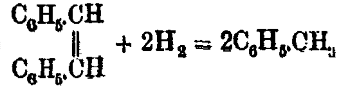
Exists in coal-tar, from which it is obtained by boiling the portion between 320° to 360° with alcohol. The cold solution is filtered, the alcohol distilled off, and the residue subjected to the same treatment until the hydrocarbon melts at about 100°. It is purified by converting it into the picric acid compound, which is recrystallized from hot alcohol and decomposed with ammonia.

Phenanthrene forms rather large plates, exhibiting a faint blue fluorescence. It melts at 100°, and begins to sublime, but boils only at 340°; it is readily soluble in alcohol, ether, acetic acid, and benzene.

Phenanthrene has been obtained synthetically together with toluene by passing stilbene through a red-hot tube:—

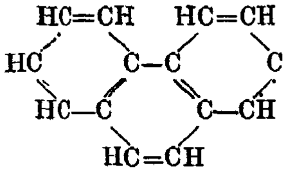
(1)


$$\begin{matrix}C_6H_5.CH\\ \Vert\\ C_6H_5.CH\end{matrix} = \begin{matrix}C_6H_4-CH\\ |\qquad\Vert\\ C_6H_4-CH\end{matrix} + H_2$$

(2)


$$\begin{matrix}C_6H_5.CH\\ \Vert\\ C_6H_5.CH\end{matrix} + 2H_2 = 2C_6H_5.CH_3$$

This synthesis, as well as the whole chemical character of phenanthrene, shows that its stands in the same relation to naphthalene as the latter to benzene, and its constitution may therefore be expressed by the following graphical formula:—



When phenanthrene and picric acid are dissolved in hot alcohol, the compound $C_{14}H_{10} + C_6H_2(NO_2)_3OH$ crystallizes on cooling in long golden-yellow prisms, melting at 145°.

Tetrahydrophenanthrene $C_{14}H_{14}$ is obtained by heating phenanthrene with concentrated hydriodic acid, and amorphous phosphorus to 240°. It is a liquid, having a faint but peculiar smell, and boiling between 300° to 310°.

Octohydrophenanthrene $C_{14}H_{18}$ is formed by using an excess of phosphorus, and heating above 240°; it is a liquid, boiling below 300°.

Phenanthrene Dibromide $C_{14}H_{10}Br_2$ is obtained by mixing well-cooled solutions of the hydrocarbon and bromine in carbon disulphide. It forms well-defined four-sided prisms, which, even in closed vessels, gradually undergo spontaneous decomposition.

Monobromophenanthrene $C_{14}H_9Br$ is produced by heating the dibromide, or by boiling it with alcohol. It forms thin white prisms, melting at 63°; on adding bromine to its solution in carbon sulphide it is converted into:—

Dibromophenanthrene $C_{14}H_8Br_2$, crystallizing in white warty needles.

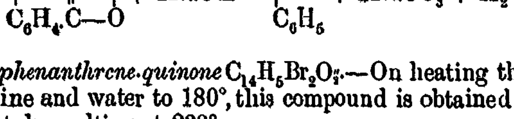
Tribromophenanthrene $C_{14}H_7Br_3$ is produced by heating the solution with bromine; it forms silky needles, melting at 126°.

Mononitrophenanthrene $C_{14}H_9.NO_2$ is formed by dissolving phenanthrene in cold concentrated nitric acid; on adding water, it is obtained as a yellow crystalline precipitate, melting between 70° and 80°.

Dinitrophenanthrene $C_{14}H_8(NO_2)_2$ is produced when the nitric acid is heated to 100°; it separates from glacial acetic acid in yellow crystals, melting between 150° to 160°.

Phenanthrenesulphonic Acid $C_{14}H_9.SO_3H$ is prepared by heating phenanthrene with sulphuric acid to 100°. Its lead-salt is soluble in water; by decomposing it with hydrogen sulphide, the pure acid is obtained. It is more freely soluble in hot than in cold water, and forms a crystalline mass.

Phenanthrene-quinone $C_{14}H_8O_2$ is produced by heating the hydrocarbon with glacial acetic acid and chromic trioxide. It crystallizes from acetic acid in orange-red, long prisms, melting at 205°, and boiling above 360°. By heating it with zinc-dust it is reduced to phenanthrene, and by passing it over red-hot soda-lime it is converted into diphenyl:—



$$\begin{array}{l} C_6H_4.C—O \\ \mid \quad\;\; \| \quad \mid \\ C_6H_4.C—O \end{array} + 4NaOH = \begin{array}{l} C_6H_5 \\ \mid \\ C_6H_5 \end{array} + 2NaCO_3 + H_2$$

Dibromophenanthrene-quinone $C_{14}H_5Br_2O_2$.—On heating the quinone with bromine and water to 180°, this compound is obtained in yellow, warty crystals, melting at 230°.

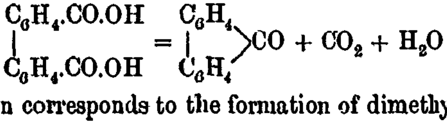
Dinitrophenanthrene-quinone $C_{14}H_6(NO_2)_2O_2$ is produced by boiling the quinone with a mixture of concentrated nitric and sulphuric acids. It crystallizes from acetic acid in yellow silky plates, melting above 280°.

Phenanthrene-hydroquinone $C_{14}H_8(OH)_2$ is readily obtained in colourless crystals by heating the quinone with aqueous sulphurous acid. It is very readily oxidized, being first converted into a dark-brown quinhydrone, and then into the quinone. By heating it with acetic anhydride it yields the compound $C_{14}H_8(OC_2H_3O)_2$, crystallizing from benzene in colourless plates, melting at 202°.

Phenanthrene-quinone-sodium Sulphite $C_{14}H_8\left\{\begin{matrix}OH\\ OSO_3Na\end{matrix}\right. + 2H_2O$.—The quinone dissolves readily in a warm solution of acid sodium sulphite, and, on cooling, this compound crystallizes out in colourless plates; it is easily decomposed by alkalis and acids.

By means of this reaction the crude quinone can be easily purified, and it may also be used for detecting the presence of phenanthrene in coal-tar. This is done by oxidizing the portion boiling between 310° to 350° with glacial acetic acid and chromic trioxide, and treating the product, first with soda to remove acids, and then with a solution of acid sodium sulphite, which dissolves only phenanthrene-quinone; on adding hydrochloric acid to the solution, the quinone is re-precipitated, and can be recognized by its properties.

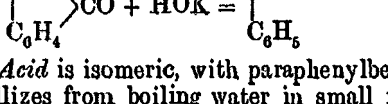
Diphenic Acid $C_{12}H_8(CO_2H)_2$ is formed by boiling the quinone for some time with dilute sulphuric acid and potassium dichromate. It crystallizes from hot water in transparent compact prisms, melting at 226°, and subliming in long transparent needles. By heating it with lime it is resolved into water, carbon dioxide, and diphenylene ketone:—



$$\begin{array}{l}C_6H_4.CO.OH\\ |\\ C_6H_4.CO.OH\end{array} = \begin{array}{l}C_6H_4\\ |\\ C_6H_4\end{array}\!\!>CO + CO_2 + H_2O$$

This reaction corresponds to the formation of dimethyl ketone from acetic acid.

Diphenyl Ketone crystallizes from alcohol in large, pale-yellow, transparent plates, melting at 84°, and boiling above 300°. By adding it gradually to fused potash, it combines with it, forming the potassium salt of a phenyl-benzoic acid:—



$$\begin{array}{l}C_6H_4\\ |\\ C_6H_4\end{array}\!\!>CO + HOK = \begin{array}{l}C_6H_4.CO.OK\\ |\\ C_6H_5\end{array}$$

Phenylbenzoic Acid is isomeric, with paraphenylbenzoic acid (page 425), and crystallizes from boiling water in small ramified needles, resembling hoar-frost, and melting at 110°. On cooling the fused acid quickly, it is obtained as a viscid, transparent mass, which remains in that state for days, but becomes crystalline again by stirring it up with a platinum-wire. By heating the acid with lime, diphenylene ketone is regenerated, while, by distilling the calcium-salt, diphenyl is formed.

ANTHRACENE-GROUP.

ANTHRACENE $C_{14}H_{10}$.

THIS isomeride of phenanthrene is obtained on the large scale by the fractional distillation of the higher-boiling portion of coal-tar, collecting that boiling at about 360°; a semi-solid mass is thus obtained, which is well pressed to remove oily substances. Crude anthracene is further purified by washing with carbon disulphide and re-crystallization from alcohol or benzene, or by sublimation.

It crystallizes in monoclinic plates, exhibiting, when quite pure, a fine blue fluorescence; it is not very soluble in alcohol, more freely in benzene, melts at 213°, and boils a little above 360°. With picric acid it forms the compound $C_{14}H_{10} + C_6H_2(NO_2)_3OH$, crystallizing in beautiful red needles.

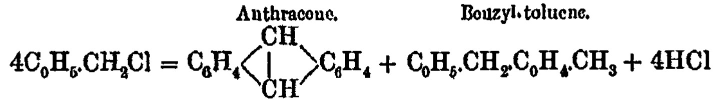
Anthracene has been obtained synthetically by three reactions:—

(1.) It is formed together with benzyl-toluene when benzyl chloride is heated with water in sealed tubes to 180°.

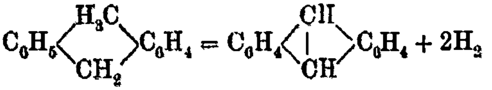
(2.) By passing benzyl-toluene through a red-hot tube, it is resolved into anthracene and hydrogen; this reaction takes place at a lower temperature if lead oxide be present.

(3.) By passing the liquid tolyl-phenyl ketone over red-hot zinc-dust.

These syntheses are explained by the following equations:—

(1) 

$$4C_6H_5.CH_2Cl = C_6H_4\left\langle\begin{matrix}CH\\|\\CH\end{matrix}\right\rangle C_6H_4 + C_6H_5.CH_2.C_6H_4.CH_3 + 4HCl$$

(2) 

$$C_6H_5\left\langle\begin{matrix}H_3C\\ \\CH_2\end{matrix}\right\rangle C_6H_4 = C_6H_4\left\langle\begin{matrix}CH\\|\\CH\end{matrix}\right\rangle C_6H_4 + 2H_2$$

Paranthracene is formed by exposing a cold saturated solution of anthracene to the sunshine; it separates out in plates, which are very sparingly soluble in alcohol and benzene. It is not acted upon by nitric acid or bromine, and melts only at 244°, being at the same time reconverted into anthracene.

Iso-anthracene.—This second isomeride of anthracene has been obtained together with amido-anthracene by the action of tin and hydrochloric acid on red nitro-anthracene. It is almost insoluble in cold alcohol, a little more freely in hot alcohol, and readily in benzene, and crystallizes in small silky plates, melting at 247°, and exhibiting a blue fluorescence. It differs from paranthracene by not being reconverted into anthracene, even if heated to 300°, and by yielding substitution-products with nitric acid.

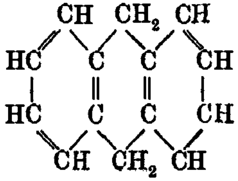
HYDRO-ANTHRACENES.

Dihydro-anthracene $C_{14}H_{12}$.—Whilst phenanthrene and naphthalene are not changed by boiling their alcoholic solutions with sodium-amalgam, anthracene is, under these conditions, converted into dihydro-anthracene. It is readily soluble in alcohol, and crystallizes in monoclinic plates, melting at 106°, and boiling at 305°, but subliming at a lower temperature in brilliant needles. When heated to a dull-red heat, it is resolved into anthracene and hydrogen.

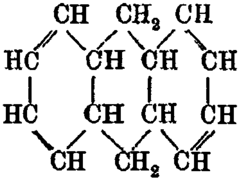
Hexahydro-anthracene $C_{14}H_{10}$ is obtained by heating dihydro-anthracene with fuming hydriodic acid and amorphous phosphorus to 200°. It dissolves freely in alcohol, and crystallizes in small plates, melting at 63°, and boiling at 290°. At a red-heat it is decomposed into hydrogen and anthracene.

The constitution of these hydrides is explained by the following graphical formula:—

Dihydro-anthracene.



Hexahydro-anthracene.



CHLORINE AND BROMINE DERIVATIVES.

Anthracene Dichloride $C_{14}H_{10}Cl_2$ is obtained by passing chlorine slowly over anthracene; it crystallizes from alcohol in long needles.

Monochloranthracene $C_{14}H_9Cl$ is produced at the same time, and readily obtained by heating the dichloride with alcoholic potash; it crystallizes in hard scales.

Dichloranthracene $C_{14}H_8Cl_2$.—By passing chlorine over heated anthracene, higher chlorinated products are formed. Dichloranthracene is sparingly soluble in alcohol, but freely in benzene. It crystallizes in long yellow needles, melting at 209°; its solutions exhibit a splendid blue fluorescence.

Tetrachloranthracene $C_{14}H_6Cl_4$ is but sparingly soluble in alcohol, and crystallizes from benzene in yellow needles.

Dibromanthracene $C_{14}H_8Br_2$ is the only compound formed when bromine is added to a solution of anthracene in carbon disulphide. It crystallizes from petroleum-naphtha in golden-yellow needles, and can be sublimed.

Dibromanthracene Tetrabromide $C_{14}H_8Br_6$ is formed when the preceding compound is exposed to gaseous bromine, and crystallizes from hot benzene in hard, colourless needles. By the action of heat it is resolved into bromine, hydrobromic acid, and *tribromanthracene* $C_{14}H_7Br_3$.

Tetrabromanthracene $C_{14}H_6Br_4$ is a body resembling the di- and tri-bromo-compound, and obtained by the action of hot alcoholic potash on dibromanthracene tetrabromide.

NITRO- AND AMIDO-COMPOUNDS.

These compounds are but little known; dilute, as well as concentrated nitric acid, converts anthracene into anthraquinone, but by the action of nitric acid on an alcoholic solution of anthracene the following nitro-compounds have been obtained.

Red Nitro-anthracene $C_{14}H_9NO_2$ is insoluble in cold alcohol, and crystallizes from hot alcohol in red needles. When treated with tin and hydrochloric acid, it yields iso-anthracene and *amido-anthracene* $C_{14}H_9.NH_2$, which is precipitated by alkalis in yellow flakes; it is a very unstable body, turning rapidly brown in the air. It dissolves acids, but does not form definite salts.

White Nitro-anthracene is more freely soluble in alcohol than the red compound, and readily in benzene, from which it crystallizes in colourless needles.

Dinitro-anthracene $C_{14}H_8(NO_2)$ is readily soluble in hot alcohol and benzene, and sublimes in small colourless plates.

Isonitro-anthracene $C_{14}H_9.NO_2$ has been obtained by boiling iso-anthracene with nitric acid; it is sparingly soluble in alcohol, freely in benzene, and sublimes in pale-yellow needles, melting at 209°.

ANTHRACENESULPHONIC ACIDS.

Anthracenemonosulphonic Acid $C_{14}H_9.SO_3H$ is formed by dissolving anthracene in concentrated sulphuric acid at 100°; its lead salt crystallizes in yellowish-white prisms, having the composition $(C_{14}H_9.SO_3)_2Pb$. By heating anthracene with sulphuric acid to 150°, the disulphonic acid is produced.

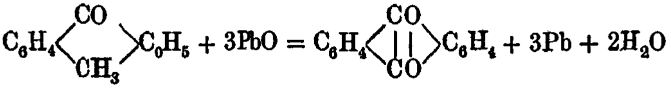
Dichloranthracenedisulphonic Acid $C_{14}H_6Cl_2(SO_3H)_2$ is obtained by heating *dichloranthracene* with fuming sulphuric acid on a water-bath. It forms orange-yellow crystals, which are soluble in water, but not in dilute acids.

ANTHRAQUINONE, OR OXYANTHRACENE $C_{14}H_8O_2$.

This compound is readily obtained by boiling anthracene with dilute sulphuric acid and potassium dichromate, or with nitric acid. It crystallizes from hot nitric acid in pale-yellow needles, melting at

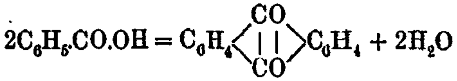
273°, and subliming, when more strongly heated, in large yellowish needles or prisms. It is a very stable body, resisting energetically the action of oxidizing agents. It differs from the isomeric phenanthrene-quinone by not being reduced by sulphurous acid, and not combining with acid sodium sulphite. When heated with a solution of soda and zinc-dust it dissolves; on adding an acid to the solution, *anthrahydroquinone* $C_{14}H_8(OH)_2$ is precipitated in yellow flakes; it is a very unstable compound, and, even in the dry state, readily oxidized to the quinone. When anthraquinone is heated with hydriodic acid and phosphorus to 150°, or when its vapour is passed over red-hot zinc-dust, it is reduced to anthracene.

Anthraquinone has been obtained synthetically by passing the liquid modification of tolyl-phenyl ketone over heated lead-oxide:—



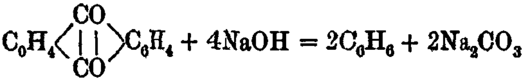
$$C_6H_4\left\langle\begin{array}{c}CO\\ CH_3\end{array}\right\rangle C_6H_5 + 3PbO = C_6H_4\left\langle\begin{array}{c}CO\\ |\,|\\ CO\end{array}\right\rangle C_6H_4 + 3Pb + 2H_2O$$

It is also formed as a bye-product in preparing benzophenone from calcium-benzoate:—



$$2C_6H_5.CO.OH = C_6H_4\left\langle\begin{array}{c}CO\\ |\,|\\ CO\end{array}\right\rangle C_6H_4 + 2H_2O$$

On the other hand, when anthraquinone is fused with caustic potash, it is resolved into two molecules of benzoic acid, and by heating it with soda-lime it yields benzene:—



$$C_6H_4\left\langle\begin{array}{c}CO\\ |\,|\\ CO\end{array}\right\rangle C_6H_4 + 4NaOH = 2C_6H_6 + 2Na_2CO_3$$

Paranthraquinone $C_{14}H_8O_2$ has been obtained by oxidizing chlorinated anthracene; it sublimes in brilliant red needles, and is converted into common anthraquinone by heating its vapour to 300°.

Iso-anthraquinone $C_{14}H_8O_2$ is formed by the oxidation of iso-anthracene, and crystallizes in beautiful red needles, melting at 235°, and dissolving in concentrated sulphuric acid with a pure indigo-blue colour.

Dichloranthraquinone $C_{14}H_6Cl_2O_2$ has been prepared by the action of chromic acid on tetrachloranthracene; it forms yellow needles.

Dibromanthraquinone $C_{14}H_6Br_2O_2$ is produced by the action of bromine on the quinone, as well as by oxidizing tetrabromanthracene. It forms yellow needles, subliming without decomposition.

Mononitro-anthraquinone $C_{14}H_7(NO_2)O_2$ is formed by boiling anthraquinone with ten parts of concentrated nitric acid for half an hour. It is a pale-yellow powder, subliming in delicate needles, melting at 230°.

a Dinitro-anthraquinone $C_{14}H_6(NO_2)O_2''$ is obtained by boiling anthraquinone with concentrated nitric acid or a mixture of sulphuric and nitric acids for some hours. It is a pale-yellow substance, subliming above 250° in yellow needles.

β Dinitro-anthraquinone.—This body is obtained, but only in a small quantity, together with anthraquinone, when anthracene is boiled with common nitric acid. It crystallizes in yellow needles, and forms with anthracene a compound, crystallizing from benzene in splendid violet plates. It also combines with other hydrocarbons; all these compounds crystallize well, and are distinguished by their brilliant colours.

Amido-anthraquinone $C_{14}H_7(NH_2)O_2''$ has been prepared by heating nitro-anthraquinone with a solution of sodium hydrosulphide. It is a bright brick-red powder, melting at 256°, and subliming in small needles. It does not appear to combine with acids.

Diazo-anthraquinone Nitrate $C_{14}H_7O_2''N_2''.NO_3$ is thrown down as a pale-red powder when nitrogen trioxide is passed into a solution of the amide in ether-alcohol.

Diamido-anthraquinone $C_{14}H_6(NH_2)_2O_2''$.—By heating *a* dinitro-anthraquinone with an alkaline solution of stannous chloride or sodium hydrosulphide, it dissolves with a green colour, and soon the diamido-compound separates out as a vermilion-red colour, subliming in beautiful garnet-red needles having a beetle-green lustre.

Anthraquinone-monosulphonic Acid $C_{14}H_7(SO_3H)O_2''$ is formed by heating anthraquinone with concentrated sulphuric acid to 250°. It is more freely soluble in water than in dilute acids, and crystallizes in yellow plates. The barium salt $(C_{14}H_7O_2''SO_3)_2Ba + H_2O$ is not very soluble in water, and forms indistinct plates. The calcium salt $(C_{14}H_7O_2''SO_3)_2Ca$ is much more freely soluble, and does not crystallize well.

Anthraquinone-disulphonic Acid $C_{14}H_6O''(SO_3H)_2$ is obtained by dissolving anthracene in five parts of sulphuric acid at 280°. It is more soluble than the monosulphonic acid, and forms yellow crystals. Its salts do not crystallize well.

This acid is also obtained by oxidizing dichlor- or dibromanthracene-disulphonic acids:—

$$C_{14}H_6Cl_2(SO_3H)_2 + O_2 = C_{14}H_{16}O_2''(SO_3H)_2 + Cl_2$$

or by heating dichlor- or dibromanthracene with sulphuric acid:—

$$C_{14}H_6Cl_2(SO_3H)_2 + SO_4H_2 = C_{14}H_6(O_2'')(SO_3H)_2 + SO_2 + 2HCl$$

The same acid has been produced by heating anthracene-disulphonic acid with manganese dioxide and dilute sulphuric acid.

OXYANTHRAQUINONES.

The following phenols of anthraquinone are known, and although they have not all been obtained from anthraquinone, they are derivatives of this body; this is shown by the fact that red-hot zinc-dust reduces them to anthracene.

Monoxyanthraquinone $C_{14}H_7O_2''(OH)$ is produced by fusing the monosulphonic acid with caustic potash. It is sparingly soluble in water, and readily in alcohol, and sublimes in lemon-yellow plates. It dissolves in alkalis with a reddish-yellow colour; the barium salt crystallizes from hot water in microscopic yellow needles, consisting of $C_{14}H_7(O_2'')O)_2Ba + H_2O$.

Monoxyanthraquinonesulphonic Acid $C_{14}H_6O_2''(OH)SO_3H$ is formed when anthraquinonedisulphonic acid is fused with potash until the blue mass which is first formed assumes a violet tinge. The free acid forms yellow crystals, and forms two series of salts; those containing one equivalent of a metal have a yellowish-red colour, and those with two equivalents are blue.

DIOXYANTHRAQUINONES $C_{14}H_6O_2''\left\{\begin{matrix}OH\\OH\end{matrix}\right.$.

Alizarin.—This interesting and important compound exists in madder-root (*Rubia tinctoria*) as glucoside, called *rubianic*, or *ruberythric acid;* on boiling it with alkalis or acids it is resolved into glucose and alizarin. The same decomposition is produced by the action of a ferment contained in the root, and therefore ground madder, which has been exposed to the air for some years, contains free alizarin, which may be extracted with ether or petroleum-spirit.

Alizarin is produced artificially by fusing dibromanthraquinone, anthraquinonedisulphonic acid, dinitro- or diamidoquinone with potash until the mass has assumed a fine violet colour:—

$$C_{14}H_6O_2''\left\{\begin{matrix}Br\\Br\end{matrix}\right. + 2KOH = C_{14}H_6O_2''\left\{\begin{matrix}OH\\OH\end{matrix}\right. + 2KBr$$

On dissolving the product in water, and adding an acid, impure alizarin is obtained as a yellow precipitate.

It is also obtained by the same reaction, together with anthraquinone, by using anthraquinone-monosulphonic acid.

Artificial alizarin is now manufactured in considerable quantity.

Alizarin crystallizes from alcohol in yellowish-red needles, containing three molecules of water, which escape at 100°. By heating it strongly it sublimes in brilliant red needles. It is but slightly soluble in water, but freely in alcohol and ether.

It dissolves in ammonia with a purple colour, and in potash or soda it yields a solution which, in transmitted light, appears bluish-purple, and, in reflected light, pure blue. This solution gives a very characteristic absorption spectrum (see Fig. 14, No. 4).

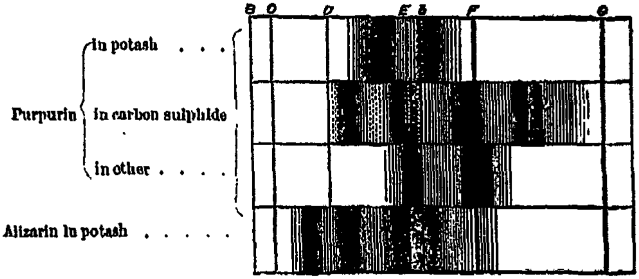


FIG. 14.

By adding barium chloride to the ammoniacal solution, a blue precipitate, consisting of $C_{14}H_6(O''_2)O_2Ba$, is obtained; calcium chloride yields a similar compound. Alum and stannic salts produce red precipitates in the alkaline solution, and ferric salts a blackish-violet one.

The property of alizarin to form insoluble coloured metallic compounds is made use of in dyeing and printing. To produce madder-colours on calico, the desired pattern is printed on the cloth as mordant. For pinks and reds, a solution of aluminium acetate (red liquor), which is thickened with gum or starch, is used; and for purples and blacks, ferrous acetate (iron-liquor) is employed, whilst a mixture of the two salts produces brown or chocolate shades. The mordanted cloth is next "aged," or hung up in a warm airy room, whereby the acetic acid is expelled, and the oxides are fixed in the fibre. The cloth is now brought into the dye-bath, consisting of boiling water and old ground madder-root; the alizarin is gradually dissolved and absorbed by the oxides.

Artificial alizarin is chiefly used for "topical" printing; for this purpose it is printed together with the mordant on the cloth, which is then "steamed" or heated to 100°; the alizarin dissolves in the free acetic acid, which soon volatilizes, whilst the alizarin combines with the oxides. The colours thus produced are more brilliant than those obtained by dyeing with madder.

To dye "Turkey-red" on cotton, the goods are mordanted with oxidised olive-oil and alum, and then brought into the dye-bath containing madder-root or alizarin; the colour thus produced contains fatty acids combined with alumina and alizarin.

When an alkaline solution of alizarin is heated with tin, it becomes yellowish-red, and contains *tetroxyanthracene* $C_{14}H_6(OH)_4$, which is precipitated by acids in yellow flakes; it readily absorbs oxygen, and is reconverted into alizarin.

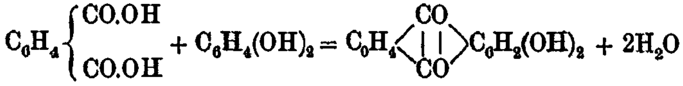
Methyl-alizarin $C_{14}H_6O''_2\left\{\begin{matrix}OH\\OCH_3\end{matrix}\right.$ is obtained by heating alizarin with methyl iodide, potash, and methyl alcohol. It forms long yellow needles, having a reddish tinge, and subliming in lustrous scales. It does not dissolve in cold alkalis, but hot potash dissolves it with a bright cherry-red colour, the compound $C_{14}H_2O''_2(OCH_3)OK$ being formed, which is also obtained in dark-red needles by adding alcoholic potash to an alcoholic solution of methyl-alizarin.

Diacetyl-alizarin $C_{14}H_6O''_2(OC_2H_3O)_2$ is prepared by heating alizarine with acetic anhydride to 160°. It crystallizes from alcohol in pale-yellow flat needles or plates, melting at 160°, and is rapidly decomposed by hot alcoholic potash.

Anthraflavin, or *Anthraflavic Acid*.—This isomeride of alizarin occurs together with oxyanthraquinone and other products in commercial artificial alizarin. It sublimes in golden-yellow needles or plates. The barium salt $2C_{14}H_6O''_2(O_2Ba) + 13H_2O$ crystallizes from hot water in reddish-brown needles.

Diacetyl-anthraflavin $C_{14}H_6O''_2(OC_2H_3O)_2$ is obtained by the action of acetic anhydride on anthraflavin at 160°. It crystallizes from glacial acetic acid in beautiful pale yellow plates or needles, melting at 228°, and is easily decomposed by alcoholic potash.

Quinizarin $C_{14}H_6O''_2(OH)_2$ is formed together with hydroquinone-phthalein (page 412), when a mixture of hydroquinone and phthalic acid is heated with sulphuric acid:—



$$C_6H_4\begin{cases}CO.OH\\CO.OH\end{cases} + C_6H_4(OH)_2 = C_6H_4\overset{CO}{\underset{CO}{\Big\langle\;|\;|\;\Big\rangle}}C_6H_2(OH)_2 + 2H_2O$$

It crystallizes from ether in yellowish-red plates, and from alcohol in deep-red needles. It dissolves in alkalis with a blue colour; and this solution gives with barium chloride a blue, and with ferric chloride a brownish-red precipitate, and with alumina it forms a red lake. Quinizarin has the greatest resemblance to alizarin, but differs from it by its absorption-spectrum, and by the strong greenish-yellow fluorescence which its solution in ether or sulphuric acid exhibits.

Chrysophanic Acid $C_{14}H_6O''_2(OH)_2$ occurs in the officinal Rhubarb-root (from one or several undefined species of *Rheum* growing in China and Central Asia), and exists also in the root of *Rumex obtusifolius*, in the lichen *Parmelia parietina*, and in the bark of *Cassia bijuga*. It is obtained by extracting rhubarb-root with ether, and crystallizes in tasteless golden-yellow needles, dissolving in alkalis with a deep-red colour; by the action of sodium-amalgam this solution becomes colourless, but assumes again the original colour in contact with air. It forms, like the other dioxy-anthraquinones, a diacetyl-compound.

Tetranitrochrysophanic Acid $C_{14}H_2O''_2(NO_2)_4(OH)_2$, or *Chrysamic*

Acid is obtained by the action of nitric acid on chrysophanic acid and on aloin (the bitter principle of aloes). It forms thin, yellow, fern-shaped crystals, resembling lead iodide, and dissolving sparingly in water with a purple colour. *Barium chrysamate* $C_{14}H_2O''_2(NO_2)_4O_2Ba + 2H_3O$ is obtained in red crystals by adding barium acetate and acetic acid to a solution of the potassium salt. *Lead chrysamate* $C_{14}H_2O''_2(NO_2)_4O_2Pb + 4H_2O$ is produced in a similar way, by using lead acetate, and forms crystals exhibiting a magnificent bronze reflection.

Hydrochrysamide $C_{14}H_2O''_2(NH_2)_3NO_2(OH)_2$.—When chrysamic acid is boiled with a solution of potassium sulphide, it dissolves with a deep-blue colour, and, on cooling, hydrochrysamide separates out in crystals, having a blue colour and copper-red reflection.

Frangulic Acid $C_{14}H_6O''_2(OH)_2$ occurs as glucoside, called *frangulin*, in the bark of *Rhamnus frangula*; on boiling it with hydrochloric acid, it splits up into glucose and frangulic acid, which crystallizes from alcohol in orange-yellow needles or quadratic plates, containing one and a-half molecules of water. It dissolves in potash with a cherry-red colour, which disappears on boiling it with zinc-dust, but comes back again in contact with the air. Barium chloride gives, with the red solution, a red precipitate.

Diacetyl-frangulic Acid $C_{14}H_6O''_2(OC_2H_3O)_2$ is formed by heating frangulic acid with acetyl chloride. It crystallizes from boiling alcohol in small, yellow, lustrous plates, melting at 184°.

TRIOXYANTHRAQUINONES $C_{14}H_5O''_2\begin{cases}OH\\OH\\OH\end{cases}$

Purpurin exists in the free state, and as glucoside, in madder-root, and may be extracted by a solution of alum, in which alizarin is insoluble. It crystallizes in yellow needles, with one molecule of water; on heating, the water is given off, and purpurin sublimes in red needles. It dissolves sparingly in water, and more freely in alcohol, with a red colour, which on adding an alkali becomes darker, but not purple. The calcium and barium salts are purple precipitates. The solutions of purpurin give different absorption-spectra (Fig. 14), which enable us not only to detect the merest trace of purpurin present in the midst of a quantity of impurities, but also to distinguish it from alizarin, which gives a totally different spectrum.

Nitric acid oxidizes purpurin to oxalic acid and phthalic acid.

Munjistin is found together with purpurin in *Munjeet*, or the Indian madder (*Rubia Munjista*). It is soluble in hot water, in alcohol, and ether; its ethereal solution exhibits a fine fluorescence, resembling that of a solution of quinizarin.

Munjistin crystallizes in yellow plates, and dissolves in alkalis with a crimson colour; it dyes on alum-mordant a light orange, and on iron-mordant a brownish-purple. The lead salt $C_{14}H_5O''_2\begin{cases}OH\\O_2Pb\end{cases}$ is an orange precipitate.

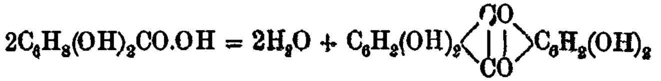
Anthrapurpurin has been found in commercial artificial alizarin, and is isolated by dissolving the crude colouring matter in dilute sodium carbonate, and agitating the liquid with precipitated alumina, which combines with the alizarin. On adding hydrochloric acid to the filtrate, anthrapurpurin, mixed with anthraflavic acid, and other bodies is precipitated, from which it is separated by boiling with alcoholic soda; anthrapurpurin forming a soda-compound, which is with difficulty soluble in alcohol. This is then dissolved in water, and barium chloride added; a purple precipitate is formed, which is washed and decomposed by an acid. It is deposited from boiling acetic acid in small groups of minute orange-coloured needles.

Anthrapurpurin dissolves in alkalis with a bluish-violet colour, and forms with alumina a red lake. It has about the same affinity for mordants as alizarin, giving similar shades, but the reds are much purer, the purples more blue, and the blacks more intense. When used to dye Turkey-red, it produces a brilliant scarlet, which is of a remarkable permanence. Its alkaline solution gives a spectrum resembling that of alizarin.

Diacetylanthrapurpurin $C_{14}H_5O''_2(OC_2H_3O)_3$ is formed by heating anthrapurpurin with acetic anhydride to 160°. It crystallizes from glacial acetic acid in beautiful pale-yellow glistening scales, melting at 221°.

TETROXYANTHRAQUINONES $C_{14}H_4O''_2\begin{cases}OH\\OH\\OH\\OH\end{cases}$

Anthrachrysone is a derivative of *a* dioxybenzoic acid, and obtained by heating this compound with sulphuric acid to 140°:—

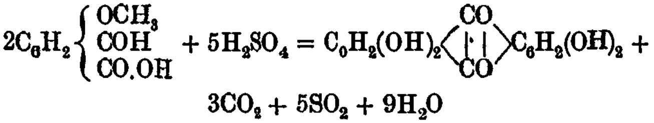


$$2C_6H_3(OH)_2CO.OH = 2H_2O + C_6H_2(OH)_2\left\langle\begin{matrix}CO\\ \mid\;\mid\\ CO\end{matrix}\right\rangle C_6H_2(OH)_2$$

It is a golden-yellow crystalline powder, which is almost insoluble in water; when heated it gives off a quinone-like smell, but does not melt at 320°. On adding barium chloride to its ammoniacal solution, the salt $C_{14}H_4O''_2(OH)_2O_2Ba$ crystallizes out in dark-red needles. The magnesium and aluminum salts are amorphous red precipitates.

Anthrachrysone dyes on iron-mordants a brown colour, and on alumina-mordants a colour like that of alizarin, but duller.

Rufiopin.—When narcotine (see Opium-alkaloids) is oxidized, it yields opianic acid, and this body is converted into rufiopine by heating it with concentrated sulphuric acid to 180°:—

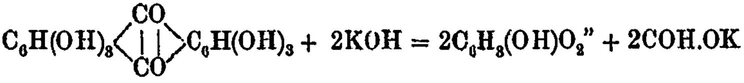


$$2C_6H_2\begin{cases}OCH_3\\ COH\\ CO.OH\end{cases} + 5H_2SO_4 = C_6H_2(OH)_2\left\langle\begin{matrix}CO\\ |\ |\\ CO\end{matrix}\right\rangle C_6H_2(OH)_2 + 3CO_2 + 5SO_2 + 9H_2O$$

Rufiopin is sparingly soluble in hot water, and separates from it in small yellow needles, and from alcohol in indistinct yellowish-red crystals. In alkalis it dissolves with a red colour, and with ammonia it forms a reddish-brown solution. Calcium chloride gives with these solutions a reddish-violet, and barium chloride a violet precipitate. On mordanted cloth it dyes colours resembling those produced by alizarin.

HEXOXYANTHRAQUINONE, OR RUFIGALLIC ACID, $C_6H_2O''_2(OH)_6$.

When gallic acid is heated with sulphuric acid in a water-bath, the liquid assumes a dark purple colour, and on adding water, a red crystalline precipitate of rufigallic acid is obtained, which on heating sublimes in yellowish-red needles. Concentrated potash colours it blue, and on addition of water it dissolves with a violet colour. It dyes mordanted cloth like alizarin, but the colours are not very brilliant. By fusing it with potash it is resolved into oxyquinone and formic acid:—

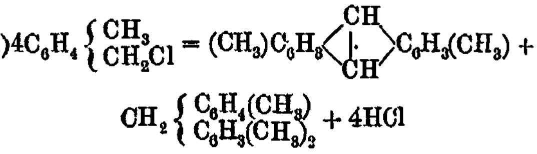


$$C_6H(OH)_3\left\langle\begin{matrix}CO\\ |\ |\\ CO\end{matrix}\right\rangle C_6H(OH)_3 + 2KOH = 2C_6H_3(OH)O_2'' + 2COH.OK$$

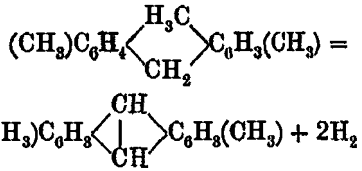
Oxyquinone forms microscopic, pale yellow needles; on adding ferric chloride to its aqueous solution, it colours first violet and then bluish-green.

DIMETHYL-ANTHRACENE $C_{14}H_8(CH_3)_2$.

When xylyl chloride is heated with water to 210°, it yields dimethyl-anthracene and the hydrocarbon $CH_2\begin{cases}C_6H_4CH_3\\ C_6H_3(CH_3)_2\end{cases}$; and the latter, when passed through a red-hot tube, is also converted into dimethyl-anthracene. These reactions are perfectly analogous to the syntheses of anthracene (page 443):—

(1)


$$4C_6H_4\left\{\begin{array}{l}CH_3\\CH_2Cl\end{array}\right. = (CH_3)C_6H_3\left\langle\begin{array}{c}CH\\|\\CH\end{array}\right\rangle C_6H_3(CH_3) + CH_2\left\{\begin{array}{l}C_6H_4(CH_3)\\C_6H_3(CH_3)_2\end{array}\right. + 4HCl$$

(2)


$$(CH_3)C_6H_4\left\langle\begin{array}{c}H_3C\\ \\CH_2\end{array}\right\rangle C_6H_3(CH_3) = (CH_3)C_6H_3\left\langle\begin{array}{c}CH\\|\\CH\end{array}\right\rangle C_6H_3(CH_3) + 2H_2$$

Dimethyl-anthracene has the greatest resemblance to anthracene; it melts at 200°, and sublimes in white plates, exhibiting a bluish-violet fluorescence.

Anthracenecarbonic Acid $C_{14}H_9.CO_2H$.—This compound stands in the same relation to anthracene as benzoic acid to benzene; it is produced by heating anthracene with carbonyl chloride to 200° for ten hours, and digesting the product with dilute sodium carbonate. It crystallizes from alcohol or hot water in needles, melting at 206°, but being slowly resolved at the same time into anthracene and carbon dioxide; this decomposition takes place quickly by heating it with soda-lime. A solution of chromic trioxide in acetic acid oxidizes it to anthraquinone:—

$$C_{14}H_9.CO_2H + 3O = C_{14}H_8O_2'' + CO_2 + H_2O$$

PYRENE $C_{16}H_{10}$.

When coal-tar is distilled until only coke is left in the retort, a yellow greasy substance passes over towards the end. By treating it with carbon disulphide, pyrene is dissolved. It is purified by recrystallizing repeatedly from alcohol, and then mixing its cold alcoholic solution with a solution of picric acid. The red crystalline precipitate $C_{16}H_{10} + C_6H_2(NO_2)_3OH$ thus obtained is decomposed with ammonia, and the hydrocarbon crystallized from alcohol.

Pyrene is obtained by the slow evaporation of its solution in rhombic plates melting at 142°.

Hexahydropyrene $C_{16}H_{10}$ is produced by heating pyrene with strong hydriodic acid and amorphous phosphorus to 150°. It crystallizes from alcohol in needles or prisms, melting at 127°, and does not combine with picric acid. At a red heat it decomposes into pyrene and hydrogen.

Nitropyrene $C_{16}H_9.NO_2$ is readily formed by heating pyrene with weak nitric acid. It separates from an alcoholic solution in yellow needles or prisms, melting at 142°.

Dinitropyrene $C_{16}H_8(NO_2)_2$ is obtained when pyrene is boiled with nitric acid of spec. grav. 1.45. It is insoluble in alcohol, and crystallizes from acetic acid in slender yellow needles.

Tetranitropyrene $C_{16}H_6(NO_2)_4$ is formed by the action of boiling concentrated nitric acid on dinitropyrene, and crystallizes from acetic acid in glistening plates or needles.

Bromine-derivatives.—When pyrene comes in contact with cold bromine-vapour, it is converted into *dibromopyrene dibromide* $C_{16}H_8Br_4$, which crystallizes from nitrobenzene in pale yellow needles. *Tribromopyrene* $C_{16}H_7Br_3$ is formed by the action of bromine on a solution of pyrene in carbon disulphide; it is almost insoluble in alcohol, ether, and carbon disulphide; from boiling nitrobenzene it crystallizes in colourless needles.

Pyroquinone $C_{16}H_8O''_2$.—To prepare this compound, pyrene is dissolved in glacial acetic acid, and solid chromic trioxide is added to the solution. It crystallizes in red needles or prisms, dissolving in concentrated sulphuric acid with a brown colour. Red-hot zinc-dust reduces it like other quinones; the hydrogen required for this reduction being furnished by zinc hydroxide, which is always present:—

$$C_{16}H_8O_2 + 3Zn + Zn(OH)_2 = C_{16}H_{10} + 4ZnO$$

CHRYSENE $C_{18}H_{12}$.

On exhausting the yellow body, which has been mentioned under pyrene, with carbon disulphide, a granular powder, resembling flowers of sulphur, and consisting of impure chrysene, is left behind. It is but sparingly soluble in the common solvents, and crystallizes from boiling alcohol in rhombic plates, melting at 250°. With picric acid it forms a compound, crystallizing from benzene in brownish-orange needles.

Nitrochrysene $C_{18}H_{11}.NO_2$ is slowly formed when chrysene is boiled with absolute alcohol and nitric acid; it forms orange crystals.

Tetranitrochrysene $C_{18}H_8(NO_2)_4$ is obtained by dissolving the hydrocarbon in fuming nitric acid as a yellow powder, which is only sparingly soluble in most solvents.

Chrysoquinone $C_{18}H_{10}O''_2$ is produced by the action of chromic trioxide on a solution of chrysene in acetic acid. It crystallizes from hot alcohol in red rhombic prisms or plates, dissolving in strong sulphuric acid with a splendid blue colour. On boiling it with potash and zinc-dust, a yellow solution is formed, from which acids precipitate *chrysohydroquinone* $C_{18}H_{10}(OH)_2$ in nearly colourless flakes; it is easily oxidized again to the quinone.

RETENE $C_{18}H_{18}$.

This hydrocarbon has been found in wood-tar from Finland; it forms colourless crystals, melting at 99°. Chromic acid oxidizes it to acetic acid, phthalic acid, and *dioxyresistene* $C_{16}H_{14}O_2$, a brick-red powder, possessing the properties of a quinone.

IDRIALENE $C_{22}H_{14}$.

The mineral *Idrialite*, occurring in the mercury-mines of Idria, is a substance resembling coal, and contains idrialene, which may be extracted by benzene. Idrialene forms small colourless plates, melting above 285°, and dissolving in concentrated sulphuric acid with a blue colour. Chromic acid converts it into *Idriaquinone* $C_{22}H_{12}O''_2$, a red crystalline solid, dissolving in sulphuric acid with a brown colour.

Idrialene is the last member of a series of hydrocarbons, which are derived from benzene by the successive addition of C_4H_2. Their chemical properties show that they must have a very similar constitution, and consist of closed chains of carbon-atoms; for oxidizing agents do not convert them into acids, like the homologues of benzene, but into quinones. The following belong to this series:—

Benzene . .	C_6H_6
Naphthalene .	$C_{10}H_8$
Phenanthrene Anthracene	$C_{14}H_{10}$
Chrysene . .	$C_{18}H_{12}$
Idrialene . .	$C_{22}H_{14}$

Pyrene does not belong to this group, but it also contains a closed chain of carbon-atoms. It is isomeric with diphenyl-diethine; both hydrocarbons contain, of all known definite carbon-compounds, relatively the largest amount of carbon, viz., 95 per cent., or even more than anthracite.

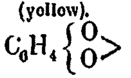
ON THE CONNECTION EXISTING BETWEEN THE COLOUR AND MOLECULAR CONSTITUTION OF CARBON-COMPOUNDS.

THE great majority of carbon-compounds is colourless; among the aromatic compounds, however, a number of bodies is found, having the characteristic colours, or possessing the property of reflecting only certain rays of light.

These coloured compounds have one property in common: they all combine with nascent hydrogen, whereby colourless bodies are produced. This proves that they contain certain atoms more closely combined than is necessary for keeping the molecule together, and therefore this closer combination must be the cause of the colouration.

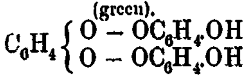
Thus the quinones of benzene and naphthalene have either a yellow or green colour, while the oxyquinones of anthracene (alizarin, &c.) are mostly red. They combine with hydrogen, forming colourless hydroquinones, and colourless compounds are also produced by combining the two atoms of oxygen with acid or alcohol-radicals. From this it appears that the combination of the oxygen-atoms is the cause of the colour:—

Quinone
(yellow).



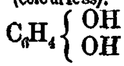
$$C_6H_4\left\{\begin{matrix}O\\O\end{matrix}\right>$$

Quinhydrone
(green).



$$C_6H_4\left\{\begin{matrix}O-OC_6H_4.OH\\O-OC_6H_4.OH\end{matrix}\right.$$

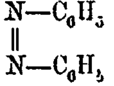
Hydroquinone
(colourless).



$$C_6H_4\left\{\begin{matrix}OH\\OH\end{matrix}\right.$$

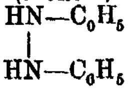
Azo-compounds have either a red or blue colour, and yield, by reduction, colourless hydrazo-compounds; their colour is, therefore, due to the double linking of the nitrogen-atoms:—

Azobenzene
(red).



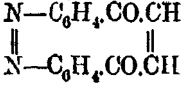
$$\begin{array}{l}N-C_6H_5\\\|\\N-C_6H_5\end{array}$$

Hydrazobenzene
(colourless).



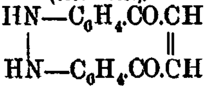
$$\begin{array}{l}HN-C_6H_5\\\ \ |\\HN-C_6H_5\end{array}$$

Indigotin
(blue).



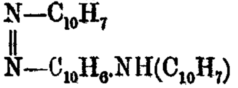
$$\begin{array}{l}N-C_6H_4.CO.CH\\\|\qquad\qquad\quad\ \|\\N-C_6H_4.CO.CH\end{array}$$

Hydro-indigotin
(colourless).



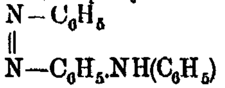
$$\begin{array}{l}HN-C_6H_4.CO.CH\\\ \ |\qquad\qquad\quad\ \ \|\\HN-C_6H_4.CO.CH\end{array}$$

Magdala-red.



$$\begin{array}{l}N-C_{10}H_7\\\|\\N-C_{10}H_6.NH(C_{10}H_7)\end{array}$$

Azodiphenyl-blue.



$$\begin{array}{l}N-C_6H_5\\\|\\N-C_6H_5.NH(C_6H_5)\end{array}$$

Similar relations exist undoubtedly between rosaniline and leucaniline, and between the phenol-colours and their products of reduction.

DESTRUCTIVE DISTILLATION.

When non-volatile carbon-compounds are heated, they undergo decomposition, and are resolved into different products, varying with the nature of the substance as well as with the mode of heating.

The destructive or dry distillation of coal, bituminous shale, wood, peat, &c., is carried on for the purpose of obtaining illuminating gas, as well as the liquid and solid products.

Crude coal-gas contains hydrogen, marsh-gas, and other paraffins, olefines, acetylene, vapour of benzene, and other volatile hydrocarbons, carbon monoxide and dioxide, carbon disulphide, hydrogen sulphide, &c.

The liquid products separate, on standing, into two layers. The aqueous solution obtained from coal contains chiefly ammonia, whilst that from wood contains methyl alcohol, acetic acid, and other fatty acids, methyl acetate, dimethyl ketone, dimethylacetal, &c.

The composition of the dark oily layer, or tar, is very varying and complicated. The following bodies have been found in different kinds of tar:—

(1.) Paraffins occur chiefly in tar which has been obtained from bodies containing a relatively large quantity of hydrogen, such as cannel and boghead-coal.

(2.) Olefines exist also principally in the same kinds of tar.

(3.) Hydrocarbon of the acetylene-series.

(4.) Benzene and methylated benzenes.

(5.) Naphthalene, acenaphthene, phenanthrene, anthracene, pyrene, chrysene, retene.

(6.) Phenol, cresol, and homologues.

Wood-tar contains also pyrocatechin and homologues, as well as their methyl-ethers (creosote).

(7.) Aniline, toluidine, and homologous bases.

(8.) Picoline and leucoline-bases.

The formation of these different bodies is partly explained by the following observations.

When a carbon-compound burns in a limited supply of air, there is always some acetylene formed, and such an incomplete combustion takes place at the beginning of the dry distillation. On exposing acetylene to a dull-red heat it undergoes polymerization, and yields benzene, styrolene, and other products, among which hydrogen and naphthalene have been observed.

At a bright-red heat, acetylene is resolved into hydrogen and carbon, but at the time some marsh-gas, ethene and naphthalene are produced.

Acetylene and hydrogen combine at a dull-red heat with the formation of ethane and ethene.

When benzene is exposed to a bright-red heat it yields diphenyl, diphenyl-benzene, and other hydrocarbons.

Toluene produces, under the same conditions, marsh-gas, benzene, naphthalene, anthracene, &c.

The xylenes and pseudocumene yield similar products, and the different hydrocarbons thus formed undergo further transformations by acting on each other at a high temperature.

GLUCOSIDES.

Nearly all plants contain peculiar compounds, which have the property in common to be resolved into a sugar, and other compounds, by the action of acids, alkalis, or ferments. Some of these glucosides occur also in the animal kingdom.

The chemical character of these bodies shows that they are compound ethers of sugar or of bodies nearly related to them, such as gum, starch, &c.

The number of glucosides known is very large, and most of them yield products of decomposition belonging to the aromatic group. We can describe here only those of more importance.

Myronic Acid $C_{10}H_{19}NS_2O_{10}$.—The potassium-salt of this acid exists in the seed of the black mustard, and is obtained by boiling the crushed seeds with alcohol, and exhausting the residue with water. It crystallizes in silky needles; on boiling it with baryta-water, or by the action of a ferment called *myrosin*, which is contained in the seed, it splits up into mustard-oil, glucose, and acid potassium sulphate:—

$$C_{10}H_{18}KNS_2O_{10} = C_4H_5NS + C_6H_{12}O_6 + HKSO_4$$

The free myronic acid, which has been prepared by decomposing the potassium-salt with tartaric acid, is a very unstable compound.

When silver nitrate is added to a solution of the potassium-salt, a white precipitate consisting of $C_4H_5NAg_2S_2O_4$ is formed, and glucose remains in solution. Hydrogen sulphide decomposes this salt into sulphur, silver sulphide, sulphuric acid, and crotonitrile:—

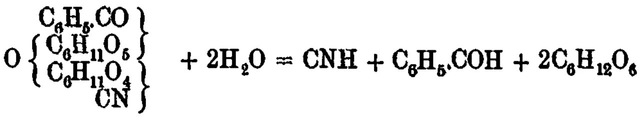
$$C_4H_5NAg_2S_2O_4 + H_2S = S + Ag_2S + H_2SO_4 + C_4H_5N$$

GLUCOSIDES OF THE AROMATIC GROUP.

Amygdalin $C_{20}H_{27}NO_{11}$ occurs in the kernels of cherries, plums, apricots, &c., and in large quantity in bitter almonds and the leaves of the common laurel; it exists also in the leaves of the bird-cherry (*Prunus Padus*) and the sprouts and bark of the mountain-ash, and in other plants belonging to the family of *Drupaceæ* and *Amygdaleæ*.

To prepare it, the paste of bitter almonds, from which the oil has been expressed, is exhausted with boiling alcohol, the solution concentrated, and the amygdalin precipitated by adding ether. It is thus obtained in pearly scales, crystallizing from water in transparent prisms with three molecules of water.

When amygdalin is treated with dilute acids, or when *emulsin* (the ferment of bitter almonds) is added to the aqueous solution, it splits up into prussic acid, benzaldehyde, and glucose :—

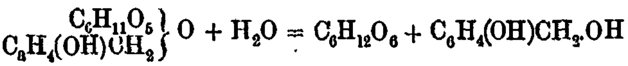


$$O\left\{\begin{matrix} C_6H_5.CO \\ C_6H_{11}O_5 \\ C_6H_{11}O_4 \\ CN \end{matrix}\right\} + 2H_2O = CNH + C_6H_5.COH + 2C_6H_{12}O_6$$

Emulsin loses its active properties when heated to 100° ; therefore in preparing oil of bitter almonds the paste must be mixed with cold water, and allowed to stand for some time before it is distilled.

Salicin $C_{13}H_{18}O_7$ is found in the young bark of several species of willow and poplar, and in castoreum (the preputial follicles of the beaver). It is obtained by exhausting the bark with boiling water, and digesting the concentrated solution with lead oxide, to remove gum, tannic acid, &c. After filtering, the liquid is treated with hydrogen sulphide, and the clear solution evaporated to the consistency of a syrup. On standing, salicin crystallizes out in colourless prisms, melting at 198°, and possessing a bitter taste.

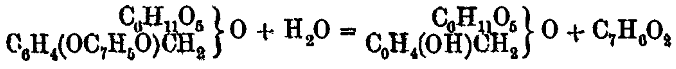
By the action of emulsin or saliva on its aqueous solution it is resolved into glucose and saligenin, or salicyl alcohol:—



$$\left.\begin{matrix} C_6H_{11}O_5 \\ C_6H_4(OH)CH_2 \end{matrix}\right\} O + H_2O = C_6H_{12}O_6 + C_6H_4(OH)CH_2.OH$$

Chromic acid-solution oxidizes it to salicylaldehyde, formic acid and carbon dioxide.

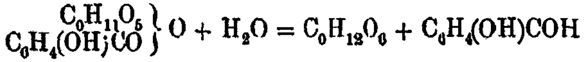
Populin $C_{20}H_{22}O_8 + 2H_2O$ occurs with salicin in the barks and leaves of the aspen, and is separated from salicin by precipitating it with potassium carbonate from the aqueous solution. It crystallizes in small prisms having a sweet taste. Boiling baryta-water resolves it into salicin and benzoic acid :—



$$\left.\begin{matrix} C_6H_{11}O_5 \\ C_6H_4(OC_7H_5O)CH_2 \end{matrix}\right\} O + H_2O = \left.\begin{matrix} C_6H_{11}O_5 \\ C_6H_4(OH)CH_2 \end{matrix}\right\} O + C_7H_6O_2$$

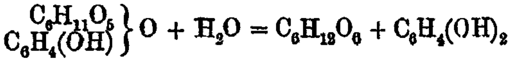
Populin has been produced artificially by the action of benzoyl chloride on salicin.

Helicin $C_{13}H_{16}O_7$ is obtained by oxidizing salicin with dilute nitric acid. It is a crystalline substance, having a slightly bitter taste. By treating it with emulsin or dilute acids it yields glucose and salicylaldehyde :—



$$\left.\begin{matrix} C_6H_{11}O_5 \\ C_6H_4(OH)CO \end{matrix}\right\} O + H_2O = C_6H_{12}O_6 + C_6H_4(OH)COH$$

Arbutin $C_{12}H_{16}O_7$ exists in the leaves of the bearberry (*Arbutus Uva-ursi*), from which it is obtained in the same way as salicin from willow-bark. It is freely soluble in water, and crystallizes in needles having a bitter taste. Emulsin or dilute acids decompose it into glucose and hydroquinone :—



$$\left.\begin{matrix}C_6H_{11}O_5\\C_6H_4(OH)\end{matrix}\right\}O + H_2O = C_6H_{12}O_6 + C_6H_4(OH)_2$$

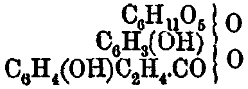
Concentrated nitric acid converts it into dinitro-arbutin, which by boiling dilute sulphuric acid is resolved into glucose and dinitrohydroquinone.

Phlorizin $C_{21}H_{24}O_{10} + 2H_2O$ occurs in the root-bark of the apple, pear, plum, and cherry-tree, and is obtained by exhausting the bark with hot dilute alcohol. It crystallizes from boiling water in silky needles, possessing a bitter taste. On heating it loses water and melts at 108°. On boiling it with dilute acids it splits up into glucose and phloretin:—

$$C_{21}H_{24}O_{10} + 2H_2O = C_6H_{12}O_6 + C_{15}H_{12}O_6$$

Phloretin $C_{15}H_{11}O_6$ forms crystalline scales; boiling alkalis decompose it into phloretic acid $C_6H_4(OH)C_3H_5O_2$ (page 395) and phloroglucin $C_6H_3(OH)_3$ (page 344).

Phlorizin has therefore the following constitution:—



$$\begin{matrix}C_6H_{11}O_5\\C_6H_3(OH)\\C_6H_4(OH)C_2H_4.CO\end{matrix}\begin{matrix}\left.\right\}O\\\left.\right\}O\end{matrix}$$

Æsculin $C_{21}H_{24}O_{13}$ exists in the bark of the horse-chestnut and other trees of the genera *Æsculus* and *Pavia*. It is sparingly soluble in cold and more freely in hot water, and crystallizes in colourless needles having a bitter taste. Its aqueous solution, even if very dilute, exhibits a beautiful sky-blue fluorescence. By boiling dilute acids or emulsin it is decomposed into glucose and æsculetin:—

$$C_{21}H_{24}O_{13} + 3H_2O = 2C_6H_{12}O_6 + C_9H_6O_4$$

Æsculetin $C_9H_6O_4$ is also found in the free state in the bark of the horse-chestnut. It is sparingly soluble in water, and forms needles having a bitter taste. Boiling potash decomposes it into formic acid, oxalic acid, and protocatechuic acid $C_6H_3(OH)_2CO_2H$.

Quercitrin $C_{33}H_{30}O_7$ is the colouring matter of "quercitron" (the bark of *Quercus tinctoria*), and occurs also in the flowers of the horse-chestnut. It is sparingly soluble in water, and forms small yellow crystals. By boiling it with dilute sulphuric acid it yields isodulcite (page 280) and *quercetin*.

Quercetin, or *Flavin* $C_{27}H_{28}O_{12}$, exists also in the free state in the common heather, in tea, and the root-bark of several trees. It is sparingly soluble in water, and sublimes in yellow needles. When it is heated with caustic potash different products are formed, among which have been found phloroglucin, protocatechuic acid, and *quercimeric acid* $CH_3(OH)(CO_2H)_2$, which crystallizes in thick prisms, and gives with ferric chloride a bluish-black colour.

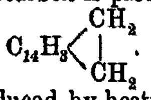
The following compounds have great resemblance to quercitrin; they yield as products of decomposition quercetin and peculiar sugars, which are different from isodulcite. *Rutin* exists in capers and the common rue; *Melin* is the colouring matter of Persian berries, and *Robinin* occurs in *Robinia pseud-acacia.*

Carminic Acid $C_{17}H_{18}O_{10}$ is found in cochineal and in the flowers of *Monarda didyma.* It is prepared by exhausting cochineal with boiling water, and precipitating the solution with lead acetate. The precipitate is well washed, and decomposed by hydrogen sulphide; on evaporating the filtrate at a low temperature, carminic acid is obtained as an amorphous brownish-purple mass. Its salts are purple or red; the splendid pigment "carmine" is the aluminium-compound.

When carminic acid is boiled with dilute sulphuric acid it is resolved into a non-fermentable sugar and *carmin-red* $C_{11}H_{12}O_7$, which is a weak acid, and dissolves in water with a red colour.

When heated with strong nitric acid, carminic acid yields oxalic acid and *nitrococcusic*, or *trinitrocresotic acid* $C_6(NO_2)_3OH\left\{\begin{matrix}CH_3\\CO_2H\end{matrix}\right.$ + H_2O, crystallizing in large silvery plates, and forming very explosive salts. On heating it with water to 180° it is resolved into carbon dioxide and *trinitrocresol*, which is identical with that obtained from coal tar-cresol.

By fusing carminic acid with potash it yields acetic, oxalic, and succinic acids and *coccinin* $C_{14}H_{12}O_5$, a yellow crystalline body.

Ruficoccin $C_{10}H_{10}O_6$ is obtained by heating carminic acid (or carmine) with sulphuric acid to 140°. It is a red crystalline powder, which, when heated with water under pressure, is converted into orange-red needles, and dissolves in alkalis with a red colour. By heating it with zinc-dust the hydrocarbon $C_{16}H_{12}$ is obtained, subliming in white plates, melting at 188°, and yielding by oxidation a yellowish-white quinone. This hydrocarbon is probably a derivative of anthracene, having the constitution  $C_{14}H_8{<}\begin{array}{l}CH_2\\ |\\ CH_2\end{array}$.

Ruficarmin $C_{16}H_{12}O_6$ has been produced by heating carmine with water to 200°. It is a carmine-red powder, which is insoluble in water but dissolves freely in alcohol.

Indican $C_{52}H_{62}N_2O_{34}$ occurs in all the plants yielding indigo, and sometimes in urine, and forms a pale-brown syrupy liquid, having a bitter taste. By the action of ferments or dilute acids it is decomposed into indigotin, a kind of sugar, and other products.

Frangulin $C_{20}H_{20}O_{10}$ is prepared by exhausting the bark of *Rhamnus frangula* with alcohol. It is a lemon-yellow crystalline powder, which dissolves in alkalis with an intense cherry-red colour, and is by boiling hydrochloric acid resolved into glucose and frangulic acid (page 451):—

$$C_{20}H_{20}O_{10} = C_{14}H_8O_4 + C_6H_{12}O_6$$

Rubianic Acid, or *Ruberythric Acid* $C_{26}H_{28}O_{14}$, exists in the fresh madder-root and in *Morinda citrifolia.* It is obtained by exhausting the root with water, and adding lead acetate to the solution to precipitate several acids and other bodies. The filtrate gives with basic lead acetate a precipitate of lead rubianate, which is decomposed by hydrogen sulphide. It crystallizes in silky yellow needles; by boiling it with dilute alkalis or acids it is resolved into alizarin and glucose. The same decomposition is caused by the action of a ferment, which is contained in the root, and has been called *erythrozyme*:—

$$C_{14}H_6O_2''\left\{\begin{matrix}OC_6H_{11}O_5\\OC_6H_{11}O_5\end{matrix}\right. + 2H_2O = 2C_6H_{12}O_6 + C_{14}H_6O_2''\left\{\begin{matrix}OH\\OH\end{matrix}\right.$$

TANNIC ACIDS.

These compounds form a group of bodies which are widely diffused through the vegetable kingdom. They are soluble in water, and have an acid reaction and a very astringent taste. With ferric chloride they yield bluish-black or green precipitates, and with gelatin they form an insoluble compound. They also combine with animal skin, which thereby acquires the property of resisting putrefaction. For these reasons tannic acids or the materials in which they occur are largely employed in the preparation of leather, ink, in dyeing and printing, &c.

Tannin, or *Gallotannic Acid*, occurs in quantity in nutgalls, and exists also in sumach (*Rhus coriaria*) and some other plants. To prepare it, powdered nutgalls are exhausted with commercial ether; the solution soon separates into two layers, the upper one consisting chiefly of ether, and the lower one of a syrupy solution of tannin in water, containing some ether. On evaporation, tannin is left behind as an amorphous, porous, and friable mass. It is freely soluble in water, less in alcohol, and only sparingly in ether. With ferric salts it gives a bluish-black precipitate, and with tartar-emetic a white one. It precipitates also the solutions of most alkaloids, of starch, gelatin, albumen, &c.

When tannin is boiled with a dilute mineral acid it assimilates water, and yields gallic acid and glucose. The same decomposition takes place when powdered nutgalls are moistened with water and exposed to the air.

The formation of gallic acid is generally explained by the equation:—

$$C_{27}H_{22}O_{17} + 4H_2O = C_6H_{12}O_6 + 3C_7H_6O_5$$

Recent researches have however shown that commercial tannin contains a large quantity of digallic acid (page 373), which by the assimilation of water is also converted into gallic acid. On the other hand, there cannot be any doubt that tannin contains a glucoside of gallic acid or digallic acid, because sugar has been obtained from it, and alcohol is formed by the fermentation of nutgalls.

Caffetannic Acid $C_{15}H_{18}O_8$ exists in coffee and Paraguay tea; it is a yellow brittle mass, which does not precipitate a solution of gelatin, and gives with ferric chloride a green precipitate. On boiling it with potash it yields a sugar and caffeic acid $C_6H_3(OH)_2C_2H_2.CO_2H$ (page 397).

Quinotannic Acid is a substance resembling tannin, and exists in combination with quinine and other alkaloids in Cinchona-barks. It gives with ferric chloride a green precipitate, and on boiling it with an acid it yields a sugar and *cinchona-red* $C_{28}H_{22}O_{14}$, which also occurs in the free state in the barks; it is a brownish-red amorphous body, having acid properties. By fusing it with potash it yields acetic acid and protocatechuic acid.

Quercotannic Acid is found in the bark of the oak, and forms a yellowish-brown mass, which precipitates ferric salts deep-blue, and is resolved by boiling dilute acids into a sugar and amorphous *quercus-red;* on fusing this body with potash, phloroglucin and protocatechuic acid are produced.

Similar tannic acids occur in the roots of *Tormentilla officinalis, Krameria triandra,* and *Aspidium Filix-mas.* They are resolved by dilute acids into sugars and red amorphous bodies, yielding, by fusing with potash, phloroglucin and protocatechuic acid.

Catechutannic Acid is a body resembling tannin, and is contained in "catechu," a brown extract which is prepared in India from *Acacia Catechu* and other trees. It precipitates gelatin and yields a dirty-green precipitate with ferric chloride. Catechu contains, besides this acid, a crystalline body called *catechin* $C_{19}H_{18}O_8$, which exists in larger quantity in the catechu from *Nauclea Gambir.* It colours ferric salts green, and reduces the solutions of the noble metals. When heated it yields pyrocatechin, and when fused with potash it is decomposed into phloroglucin and pyrocatechuic acid.

Kinotannic Acid forms the principal constituent of "kino," a reddish-brown extract, which is prepared from the juice of *Pterocarpus erinaceus* and *Coccoloba uvifera.* It gives with ferric salts a green precipitate, and yields phloroglucin when it is fused with potash.

Moritannic Acid, or *Maclurin* $C_{13}H_{10}O_6 + H_2O$, is the colouring matter of "fustic," or the wood of *Morus tinctoria,* and separates from a hot aqueous solution as a yellow crystalline powder. It colours ferric salts green, and is resolved by potash into phloroglucin and protocatechuic acid.

Fustic contains also *morin* $C_{12}H_8O_5$, which is sparingly soluble in water, and crystallizes in pale yellow needles. By the action of sodium-amalgam and water it is converted into phloroglucin.

$$C_{12}H_8O_5 + H_2O + H_2 = 2C_6H_6O_3$$

Scoparin $C_{21}H_{22}O_{10}$ exists in the common broom (*Spartium scoparium*), and separates from alcohol in small colourless crystals, which dissolve in alkalis with a greenish-yellow colour, and on boiling this solution down, phloroglucin and protocatechuic acid are produced.

GLUCOSIDES YIELDING PRODUCTS OF UNKNOWN CONSTITUTION.

Fraxin $C_{32}H_{86}O_2$ is found in the bark of the ash and horse chestnut-tree, and forms colourless needles, which are sparingly soluble in water, and yield a fluorescent solution. Dilute acids resolve it into sugar and crystalline *Fraxetin* $C_{10}H_8O_5$.

Pinipicrin $C_{22}H_{36}O_{11}$ is contained in the bark and needles of *Pinus sylvestris* and of *Thuja occidentalis*. It is a yellow, amorphous, bitter powder, which by dilute boiling sulphuric acid is resolved into sugar and *ericinol* $C_{10}H_{16}O$, a pale yellow oil possessing a strong aromatic smell, and which is also obtained by distilling the leaves of *Ledum palustre*, *Rhododendron ferrugineum*, *Calluna vulgaris*, and other *Ericaceæ* with water.

Convolvulin $C_{31}H_{50}O_{16}$ is the active principle of jalap, and forms a resinous mass, which is soluble in alcohol and in alkalis; the latter solution contains bibasic *convolvulic acid* $C_{31}H_{52}O_{17}$, an amorphous. sour substance, which is soluble in water. These two compounds are converted by the action of acids or emulsin into sugar and *convolvulinol* $C_{13}H_{24}O_3$, which combines with alkalis, forming monobasic *convolvulinolic acid* $C_{13}H_{26}O_4$, which is sparingly soluble in water, and crystallizes in small needles. Nitric acid oxidizes it to *ipomic acid* $C_{10}H_{18}O_4$.

Jalapin $C_{34}H_{56}O_{16}$ is a homologue of convolvulin, and exists in the jalap from *Convolvulus orizabensis*. It has great resemblance to convolvulin, yielding sugar and *jalapinol* $C_{16}H_{30}O_8$, which by alkalis is converted into *jalapinolic acid* $C_{16}H_{32}O_4$, and by nitric acid into ipomic acid.

Similar resinous glucosides exist in other plants of the same order; the root of *Ipomœa Turpethum* contains *turpethin*, and that of *Convolvulus Scammonia* a compound called *scammonin*.

Helleborein $C_{26}H_{44}O_{15}$ is contained in the root of the *Christmas-rose* (*Helleborus niger*). It crystallizes from water in small needles, and is a narcotic poison. With dilute acids it yields sugar and amorphous *helleboretin* $C_{14}H_{20}O_3$.

Helleborin $C_{36}H_{42}O_6$ is found together with some helleborein in the root of *Helleborus viridis*. It is insoluble in water, and forms glistening needles. It is a powerful poison, and by boiling it with an acid is resolved into sugar and amorphous *helleboresin* $C_{30}H_{38}O_4$.

Saponin $C_{32}H_{54}O_{18}$ is contained in the root of *Saponaria officinalis*, *Gypsophila Struthium*, *Agrostema Githago*, and different species of *Lychnis*, in *Polygala Senega*, in the seeds of the horse-chestnut, and many other plants. It is a white amorphous powder, having a sweetish astringent taste. Its dust produces violent sneezing, and its aqueous solution, when shaken, froths like a soap-solution. Fuming hydrochloric acid resolves it into an amorphous sugar and *sapogenin* $C_{14}H_{22}O_4$.

Caïncin $C_{40}H_{46}O_{18}$ is found in the caïnca-root (*Chiococca racemosa*), and crystallizes in slender prisms. Hydrochloric acid decomposes it into sugar and *caïncetin* $C_{22}H_{34}O_3$, which when fused with potash is resolved into butyric acid and *caïncigenin* $C_{14}H_{24}O_2$.

Chinovin $C_{30}H_{48}O_8$ has been found in *China nova* and other cinchona-barks. It is an amorphous powder, which is insoluble in water, and by boiling it with an acid yields mannitane and *chinovic acid* $C_{24}H_{38}O_4$, which is insoluble in water, sparingly soluble in boiling alcohol, and forms a white crystalline powder. It is a bibasic acid, and apparently homologous with the phthalic acids.

Glycyrrhicin, or *Liquorice-sugar* $C_{24}H_{36}O_9$, is the sweet principle contained in the root of the common liquorice, and is prepared by precipitating an aqueous infusion of the root with basic lead acetate, and decomposing the washed precipitate with hydrogen sulphide. It is a yellowish amorphous powder, having a sweet and acrid taste. When boiled with a dilute acid, it is resolved into sugar and resinous *glycyrretin*.

Daphnin $C_{31}H_{34}O_{19} + 4H_2O$ is found in the bark of the mezereon and other species of *Daphne*. It is almost insoluble in cold water, and crystallizes from a boiling solution in colourless prisms. Dilute acids decompose it into sugar and *daphnetin* $C_{19}H_{14}O_9$.

Digitalin is a most violent poison, existing in the common foxglove, and forms an amorphous powder having an intensely bitter taste. Its composition is not known; acids resolve it into sugar and amorphous *digitalretin*.

Antiarin is the active principle of the arrow-poison of Java, which is prepared from the milky juice of *Antiaris toxicaria*. It forms colourless crystals, and is soluble in water and alcohol. It has not been analyzed; acids convert it into sugar and a resinous substance.

Cyclamin $C_{20}H_{24}O_{10}$ occurs in the tubers of *Cyclamen europæum*, and is resolved into sugar and *cyclamiretin* $C_{14}H_{10}O_6$.

Ononin $C_{30}H_{34}O_{13}$ is contained in the root of *Ononis spinosa*, and is decomposed by boiling hydrochloric acid into sugar and *formonatin* $C_{24}H_{22}O_7$, which by alkalis is resolved into *ononetin* $C_{23}H_{22}O_6$ and formic acid.

Coniferin occurs in the cambial liquid of the *Coniferæ*, and has been resolved into sugar and a resin.

Menyanthin, which is found in *Menyanthes trifoliata*, yields with acids sugar and *menyanthol* C_8H_8O, which is a liquid resembling oil of bitter almonds, and when exposed to the air is oxidized to an acid of unknown composition.

Polychroïte $C_{48}H_{60}O_{18}$ is the colouring matter of saffron, and forms an amorphous, deliquescent, ruby-red mass. When boiled with a dilute acid it yields sugar, crocin, and a volatile oil. *Crocin* $C_{16}H_{18}O_6$

is a red powder, which is insoluble in water, but dissolves in alcohol and alkalis. The volatile yellow oil has the composition $C_{10}H_{16}O$, and smells strongly like saffron.

ANIMAL GLUCOSIDES.

Chitin $C_9H_{15}NO_6$ is the principal constituent of the horny cover of beetles and crustaceans. To prepare it, the wing-cases of the cockchafer are exhausted successively with boiling water, dilute potash, dilute hydrochloric acid, alcohol, and ether. Chitin is left behind as a colourless, translucent mass. With concentrated sulphuric acid it forms a colourless solution, which, when diluted with water and boiled, contains ammonia, a fermentable sugar, and other products.

Cerebrin $C_{17}H_{33}NO_3$ is a constituent of the brain, and prepared by exhausting brain with boiling water, which removes inosite, volatile fatty acids, lactic acids, creatine, uric acid, and other bodies. The residue is then treated with boiling ether, which dissolves cholesterin, lecithin, and cerebrin, which latter, being insoluble in cold ether, separates out on cooling. It is a light, amorphous powder, without taste or smell; with boiling water it forms a gelatinous mass, and boiling dilute acids convert it into sugar and other unknown bodies.

ARTIFICIAL BASES FROM VARIOUS SOURCES.

BASES FROM ANIMAL OIL.

Pyridine . . .	C_5H_5N	Parvoline . . .	$C_9H_{13}N$
Picoline . . .	C_6H_7N	Coridine . . .	$C_{10}H_{15}N$
Lutidine . . .	C_7H_9N	Rubidine . . .	$C_{11}H_{17}N$
Collidine . . .	$C_8H_{11}N$	Viridine . . .	$C_{12}H_{10}N$

These bases occur in "Dippel's oil" (*Oleum animale Dippelii*), which is produced by the dry distillation of bones and other animal matter, and occur also in coal-tar. They differ from the isomeric aromatic amido-compounds by being tertiary bases, which combine with the iodides of the alcohol-radicals to form compound ammonium iodides. Their hydrochlorides yield with the chloride of gold and platinum double salts which readily crystallize.

Pyridine C_5H_5N exists also in the products of combustion of tobacco; it is a limpid liquid, which is soluble in water, possesses a strong and persistent odour, and boils at 117°. It is also produced, but in a small quantity only, by treating an alcoholic solution of amido-azonaphthalene with hydrochloric acid and tin and by the action of phosphorus pentoxide on amyl nitrate:—

$$C_5H_{11}NO_3 = 3H_2O + C_5H_5N$$

It forms a sulphonic acid with fuming sulphuric acid, and by adding potash to a solution of pyridine-ethylammonium hydroxide a red body is gradually formed, dyeing a beautiful red shade on silk.

Sodium converts pyridine into bases which are richer in hydrogen, and into *dipyridine* $C_{10}H_{10}N_2$, which forms colourless crystals melting at 108°. It yields crystallizable salts, and is not acted on by concentrated nitric acid.

Picoline C_6H_7N is a liquid resembling pyridine, and boiling at 135°. It has been obtained artificially by the dry distillation of acrolein-ammonia:—

$$C_6H_9NO = C_6H_7N + H_2O$$

and by heating propenyl tribromide with alcoholic ammonia; first dimonobromallylamine is formed, which by the further action of ammonia is converted into picoline:—

$$C_6H_9Br_2N = C_6H_7N + 2HBr$$

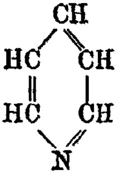
Lutidine C_7H_9N is a liquid resembling picoline, and boils at 154°.

Collidine $C_8H_{11}N_2$ is an oily liquid boiling at 176°, and possessing a powerful odour. It has been produced artificially by heating aldehyde-ammonia with absolute alcohol to 130°. In this reaction the acetaldehyde is probably first converted into crotonaldehyde, which is then transformed into collidine:—

$$2C_4H_6O_2 + NH_3 = C_8H_{11}N + 2H_2O$$

The same base has been obtained by heating ethidene dibromide with aqueous ammonia to 160°.

The other bases belonging to this group are also liquids possessing a strong odour; their constitution is not definitely known, but they contain the nitrogen only combined with carbon, and the carbon-atoms probably linked together in a closed chain; this appears the more probable as pyridine has been obtained from naphthalene, and the constitution of the first member appears to be the following:—



BASES CONTAINED IN COAL-TAR.

Leucoline . . .	C_6H_7N	Cryptidine . .	$C_{11}H_{11}N$
Iridoline . . .	$C_{10}H_6N$		

BASES FORMED BY THE DESTRUCTIVE DISTILLATION OF ALKALOÏDS.

Chinoline . . .	C_9H_7N	Pentahiroline .	$C_{13}H_{15}N$
Lepidine . . .	$C_{10}H_9N$	Isoline	$C_{14}H_{17}N$
Dispoline . . .	$C_{11}H_{11}N$	Ettidine . . .	$C_{15}H_{19}N$
Tetrahiroline . .	$C_{12}H_{13}N$	Validine . . .	$C_{10}H_{21}N$

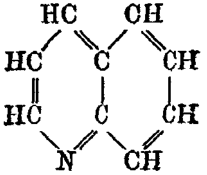
Chinoline C_9H_7N has been produced by distilling quinine, cinchonine, strychnine, and other alkaloïds with potash. It is a colourless liquid, possessing a strong aromatic odour, and boiling at 220°. Its salts are soluble in water, and crystallize well. Fuming sulphuric acid converts it into *chinolinesulphonic acid* $C_9H_6N.SO_3H$, forming hard, shining crystals, and yielding an amorphous barium salt, which is sparingly soluble in water. When bromine-vapour comes in contact with chinoline it is converted into *tribromochinoline* $C_9H_4Br_3N$, crystallizing in soft silky needles.

Cyanine $C_{28}H_{35}N_2I$.—This beautiful compound is produced by treating *chinoline-amylammonium iodide* $(C_9H_7.C_5H_{11})NI$ with caustic potash. It crystallizes in brilliant plates having a beetle-green lustre, and dissolving in alcohol with a magnificent blue colour. On dissolving it in hot hydriodic acid a colourless solution is obtained, which on cooling deposits yellow needles, containing $C_{28}H_{35}N_2I + IH$. With other acids it forms similar compounds, which are decomposed by boiling water into free acid and the coloured salt.

The homologues of chinoline are capable of producing similar blue compounds. A mixture of the chinoline and lepidine-compound was some time ago used for dyeing on silk a pure and rich blue, but its use has been abandoned, on account of it being rapidly acted upon by light and destroyed.

Leucoline was formerly believed to be identical with chinoline, from which it differs by boiling at 238°, and not yielding a blue colour with amyl iodide and potash.

Chinoline has a great resemblance with pyridine, and stands probably in the same relation to this base as naphthalene to benzene, and its constitution would therefore be:—



NATURAL BASES OR ALKALOÏDS.

Many plants, and principally those of medical or poisonous properties, contain basic compounds which are called *alkaloïds.* They contain nitrogen, and a few of them are volatile, and have great resemblance with compound ammonias; the majority, however, have a more complicated constitution, and are decomposed by heat.

Most of them are sparingly soluble in water, more freely in alcohol; the solutions have an alkaline reaction, and usually an intensely bitter taste. They combine, like ammonia, with acids, forming crystallizable salts, which are more freely soluble than the bases. Their hydrochlorides form, with the chlorides of gold, platinum, mercury, &c., crystalline double salts.

Most alkaloïds are precipitated from their solutions by tannin, the double iodides of potassium, and mercury, cadmium and bismuth, phosphomolybdic acid, phosphoantimonic acid, metatungstic acid, picric acid, and a solution of iodine in potassium iodide. By treating these precipitates with an alkali, the bases are set free, and the above reactions are therefore frequently made use of in the preparation or detection of alkaloïds.

VOLATILE ALKALOÏDS.

Conine $C_8H_{15}N$ exists in all parts of the true hemlock (*Conium maculatum*), principally in the seeds, from which it is obtained by distilling them with dilute soda-solution. The distillate is neutralized with sulphuric acid, evaporated to the consistency of a syrup, and then distilled with concentrated soda.

Conine is an oily liquid having the specific gravity 0·89, boiling at 163°·5, and turning the plane of polarization to the right. It possesses a nauseous and sharp taste and disagreeable smell; it dissolves to some extent in cold water, and this solution becomes turbid on heating it gently, conine being more soluble in cold than in warm water. When in contact with air, it colours brown, and is slowly decomposed with the formation of ammonia; the solutions of its salts undergo a similar change. On oxidation it yields butyric acid, and when nitrogen trioxide is passed into it, a yellow thick liquid is formed, which by water is decomposed into nitric acid and *azoconydrine* $C_8H_{16}(NO)N$, a pale yellow oil, which is reconverted into conine by the action of nascent hydrogen:—

$$C_8H_{16}(NO)N + 2H_2 = C_8H_{15}N + H_2O + NH_3$$

When azoconydrine is heated with phosphorus pentoxide, it is resolved into water, nitrogen, and *conylene* C_8H_{14}, which is a homologue of acetylene; it is a very refractive liquid, boiling at 126°, and forming with bromine *conylene dibromide* $C_8H_{14}Br_2$, a heavy oil, possessing a disagreeable, pungent smell. Conylene is the dyad radical of conine $C''_8H_{14}.NH$.

Methylconine $C_8H_{14}.NCH_3$ occurs sometimes in hemlock, and is readily prepared by the action of methyl iodide on conine. It has great resemblance to conine, and combines with methyl iodide, forming crystalline *conine-methylammonium iodide* $N(C''_8H_{14})(CH_3)_2I$, which by the action of moist silver oxide is converted into the caustic and alkaline hydroxide.

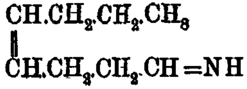
Conydrine $C_8H_{17}ON$ exists also in hemlock, and forms colourless, iridescent plates. It melts at 120°·6, boils at 225°, and sublimes readily at a lower temperature. When heated with phosphorus pentoxide it is resolved into water and conine. It forms crystalline salts, and is not acted upon by nitrogen trioxide. By treating it with ethyl iodide it forms *conydrine-diethylamine hydriodide* $N(C_8H_{16}O)(C_2H_5)_2.IH$.

Paraconine $C_8H_{15}N$.—This isomeride of conine has been produced synthetically by the action of alcoholic ammonia on butyraldehyde, which thereby is converted into *dibutyraldine* $C_{18}H_{17}ON$, which is isomeric with conydrine, and is by distillation resolved into water and paraconine.

Paraconine is a liquid boiling at 160° to 170°; its odour and taste resembling those of conine, and its aqueous solution becomes turbid on heating. Like conine, it is a powerful narcotic poison, but differs from it by being a tertiary base and possessing no rotatory power.

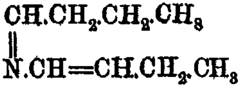
The constitution of these different compounds may be explained by the following formulæ:—

Conine.



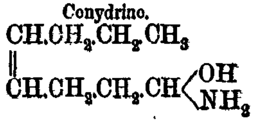
$$\begin{array}{l}\mathrm{CH.CH_2.CH_2.CH_3}\\ \|\\ \mathrm{CH.CH_2.CH_2.CH{=}NH}\end{array}$$

Paraconine.



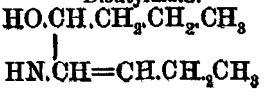
$$\begin{array}{l}\mathrm{CH.CH_2.CH_2.CH_3}\\ \|\\ \mathrm{N.CH{=}CH.CH_2.CH_3}\end{array}$$

Conydrine.



$$\begin{array}{l}\mathrm{CH.CH_2.CH_2.CH_3}\\ \|\\ \mathrm{CH.CH_2.CH_2.CH}\left\langle\begin{array}{l}\mathrm{OH}\\ \mathrm{NH_2}\end{array}\right.\end{array}$$

Dibutyraldin.



$$\begin{array}{l}\mathrm{HO.CH.CH_2.CH_2.CH_3}\\ \quad\quad\; |\\ \mathrm{HN.CH{=}CH.CH_2CH_3}\end{array}$$

Nicotine $C_{10}H_{14}N_2$ occurs in the seeds and leaves of different kinds of tobacco. The common sorts contain about 8 per cent., and Havanna tobacco only 2 per cent. To prepare nicotine, the leaves are exhausted with very dilute, warm sulphuric acid, and the concentrated solution distilled with potash. The distillate is shaken with ether, which dissolves the nicotine; on evaporation it is obtained as an oil, which is purified by distilling it over lime in a current of hydrogen.

Nicotine is a colourless oil, possessing a faint smell of tobacco in the cold, but on heating it becomes nauseous and pungent. It has the specific gravity 1·048 at 0°, and boils under decomposition at 250°, but volatilizes without change in a current of hydrogen at about 180°. It is a bi-acid base, forming salts which do not crystallize well.

Nicotine is a tertiary amine, and forms with ethyl iodide the crystalline *nicotine-ethylammonium di-iodide* $N_2(C_{10}H_{14})(C_2H_5)_2I_2$, which with moist silver oxide yields the caustic and strongly alkaline hydroxide.

It combines with bromine, forming the compound $C_{10}H_{12}Br_4N_2.BrH$, which crystallizes in light-red prisms, and is converted by boiling water into *dibromonicotine hydrobromide* $C_{10}H_{12}Br_2N_2.BrH$; by decomposing this compound with ammonia, *dibromonicotine* is obtained, crystallizing from hot water in long colourless needles.

Nicotinic Acid $C_{10}H_8N_2O_3$ is obtained by oxidizing nicotine with fuming nitric acid or chromic acid solution. It forms colourless crystals, which can be sublimed, and possesses a strongly acid taste. It forms not only metallic salts, but combines, like an amido-compound, with strong acids. The hydrochloride $2C_{10}H_8N_2O_3 + 3HCl$ forms colourless prisms, and gives with platinic chloride a double salt $4C_{10}H_8N_2O_3 + 6HCl + 3PtCl_4 + 8H_2O$, crystallizing in beautiful orange-red, oblique prisms. On distilling the calcium salt with lime, nitrogen is given off and *pyridine* distils over.

ALKALOÏDS OCCURRING IN OPIUM.

Opium is the inspissated juice of the capsulæ of the poppy (*Papaver somniferum*), and prepared in large quantity in Asia Minor, Turkey, Egypt, India, and Southern Germany. It is a very complicated substance, containing a number of alkaloïds in combination with meconic and sulphuric acids, and gummy and resinous matters, caoutchouc, &c.

The best opium from Smyrna contains about 10 per cent. of morphine. The following opium-alkaloïds are known:—

Morphine . .	$C_{17}H_{19}NO_3$	Meconidine . .	$C_{21}H_{23}NO_4$
Oxymorphine .	$C_{17}H_{19}NO_4$	Laudanosine . .	$C_{21}H_{27}NO_4$
Codeine . . .	$C_{18}H_{21}NO_3$	Rhœadine . .	$C_{21}H_{21}NO_6$
Thebaïne . . .	$C_{19}H_{21}NO_3$	Cryptopine . .	$C_{21}H_{23}NO_5$
Codamine . .	$C_{20}H_{25}NO_4$	Narcotine . . .	$C_{22}H_{23}NO_7$
Laudanine . .	$C_{20}H_{25}NO_4$	Lanthopine . .	$C_{23}H_{25}NO_4$
Protopine . . .	$C_{20}H_{19}NO_5$	Narceine . . .	$C_{23}H_{29}NO_9$
Papaverine . .	$C_{21}H_{21}NO_4$		

Of these compounds only morphine and narcotine exist in larger quantities. Opium is a most valuable medicine; when given in a small dose it acts as a sedative and anodyne, and produces a quiet sleep, although it increases the rapidity and fulness of the pulse. In larger doses it acts as a narcotic poison, producing intense sleepiness, stupefaction, and death.

The most violent poison is thebaïne; then in succession less, narceine, papaverine, codeine, morphine, and narcotine.

Morphine is prepared on the large scale by exhausting opium with a small quantity of warm water, and adding calcium chloride to the solution; a precipitate of calcium meconate and sulphate is obtained, and the solution contains the hydrochlorides of the bases. On leaving the concentrated solution to stand, the salts of morphine, codeine, and oxymorphine crystallize out, and are separated by adding ammonia to their aqueous solution, by which only morphine is precipitated.

Morphine $C_{17}H_{19}NO_3 + H_2O$ crystallizes from alcohol in shining prisms, dissolving in 1000 parts of cold and 500 parts of boiling water; it is almost insoluble in ether and chloroform, but dissolves in caustic alkalis. When heated, it loses the water of crystallization and melts, forming a colourless liquid, which on cooling solidifies to a crystalline mass.

Morphine Hydrochloride $C_{17}H_{10}NO_3.ClH + 3H_2O$ dissolves freely in alcohol and boiling water, and crystallizes in thin prisms.

Morphine Sulphate $2(C_{17}H_{10}NO_3)SO_4H_2 + 5H_2O$ is a similar body. *Morphine Acetate* is very soluble in water, and does not crystallize well.

When morphine is heated with potash, it yields methylamine. By adding ferric chloride a solution of a neutral salt of morphine of a deep-blue colour is produced, and a solution of molybdic acid in concentrated sulphuric acid gives with dry morphine, or one of its salts, a magnificent violet colour, which in the air first turns into a greenish-brown, and then becomes deep-blue. Morphine decomposes iodic acid, iodine being set free, which can easily be recognised by starch-paste. When morphine is heated with strong sulphuric acid to 100°, and a drop of nitric acid is added, the liquid assumes a deep blood-red colour.

Morphine and its salts are much used in medicine: they act more agreeably than opium, and are less exciting, and less liable to produce nausea or headache.

Apomorphine $C_{17}H_{17}NO_2$ is produced by heating morphine with a large excess of hydrochloric acid for some hours to 150°:—

$$C_{17}H_{10}NO_3 = C_{17}H_{17}NO_2 + H_2O$$

By decomposing its hydrochloride with acid sodium carbonate, the free base is obtained as a white amorphous powder, which in the air rapidly turns green. It is more freely soluble in water and ether than morphine; the green oxidized apomorphine dissolves in ether with a splendid dark-pink, and in chloroform with a violet colour.

The physiological action of apomorphine is entirely different from that of morphine; a very small dose of the hydrochloride produces speedy vomiting and considerable depression, but this soon passes off without leaving any ill effects.

Oxymorphine, or *Pseudomorphine* $C_{17}H_{19}NO_4$, does not always occur in opium, and is obtained by heating morphine hydrochloride with silver nitrite. It is a white powder, which gives reactions similar to those of morphine.

Codeine, or *Methyl-morphine* $C_{17}H_{11}(CH_3)NO_3$, is precipitated from the concentrated ammoniacal solution by caustic soda; it is freely soluble in alcohol, ether, ammonia, and boiling water, and crystallizes in large transparent octahedrons. It is also used in medicine.

When heated with an excess of hydrochloric acid on a water-bath, it is converted into *chlorocodide*:—

$$C_{18}H_{21}NO_3 + HCl = C_{18}H_{20}ClNO_2 + H_2O$$

Chlorocodide is obtained by adding an alkali to the solution of the hydrochloride as a snow-white mass, which readily dissolves in alcohol and ether. On heating the hydrochloride with water to 140°, codeine is reproduced:—

$$H_2O + C_{17}H_{17}(CH_3)ClNO_2 = HCl + C_{17}H_{17}(CH_3)(OH)NO_2$$

When chlorocodide is heated with hydrochloric acid under pressure it is resolved into methyl chloride and apomorphine:—

$$C_{17}H_{17}(CH_3)ClNO_2 = C_{17}H_{17}NO_2 + CH_3Cl$$

Narcotine $C_{19}H_{14}(CH_3)_3NO_7$ is partly left behind in the "marc," or insoluble portion of opium, from which it is extracted with acetic acid. It crystallizes in small, glistening, white prisms, melting at 170°, and is tasteless and almost insoluble in water. It dissolves readily in acids, but does not form well-defined salts.

When narcotine is heated with water to 250°, it yields trimethylamine, and by heating it with fuming hydriodic acid it is resolved into three molecules of methyl iodide and a new base called *nornacotine* $C_{19}H_{17}NO_7$. Products standing intermediate between this compound are formed by heating narcotine with hydrochloric acid; the first product being *dimethyl-nornacotine* $C_{19}H_{15}(CH_3)_2NO_7$, which by the further action of the acid is transformed into methyl-nornacotine $C_{19}H_{10}(CH_3)NO_7$.

Above 200° narcotine is resolved into meconin and cotarnine, and oxidizing agents convert it into cotarnine and opianic acid.

Cotarnine $C_{12}H_{13}NO_3$ is a base crystallizing from hot water in colourless prisms. By the continued action of hot dilute nitric acid it yields methylamine and *cotarnic acid* $C_{11}H_{12}O_5$, and concentrated sulphuric acid converts it into *apophyllenic acid* $C_8H_7NO_4$, which forms large colourless crystals.

Meconine $C_{10}H_{10}O_4$ occurs also in the free state in opium, and crystallizes from hot water in brilliant prisms melting at 110°. It has the properties of an alcohol, and forms compound ethers.

Opianic Acid $C_{10}H_{10}O_5$ forms thin prisms, which are not freely soluble in water. It has the properties of an aldehyde, and yields on oxidation *hemipinic acid* $C_{10}H_{10}O_6$, which is also obtained together with meconin when opianic acid is heated with potash-solution.

Hemipinic Acid $C_{10}H_{10}O_6$ crystallizes in large four-sided prisms, which melt at 180°, and sublime without decomposition. By heating it with concentrated hydriodic acid it yields oxalic acid, methyl iodide, and two isomeric acids $C_{14}H_{10}O_6$.

Opinic Acid crystallizes from hot water in brilliant prisms, and gives with ferric chloride a lilac colour.

Isopinic Acid forms small warty needles, dissolving more freely than opinic acid, and yielding a deep-blue colour with ferric chloride.

Thebaïne $C_{19}H_{21}NO_3$ crystallizes from dilute alcohol in plates resembling benzoic acid, and from strong alcohol in thick prisms, melting at 193°. It is a strong base and a violent poison, producing tetanus. In concentrated sulphuric acid it dissolves with a blood-red colour.

By heating it with hydrochloric acid it is converted into *thebenine hydrochloride*, crystallizing in large laminæ having a bitter taste, and consisting of $C_{19}H_{21}NO_3.ClH + 3H_2O$. On adding normal sodium sulphide to its solution, *thebenine* is obtained as a white flocculent precipitate, which rapidly oxidizes in the air. It is isomeric with thebaïne, but differs from it, by dissolving in sulphuric acid with a splendid blue colour.

Codamine $C_{20}H_{25}NO_4$ crystallizes from benzene in small prisms melting at 126°, and giving with ferric chloride or concentrated nitric acid a deep-green solution.

Laudanine $C_{20}H_{25}NO_4$ forms small prisms melting at 166°; it gives with concentrated nitric acid an orange-red solution, and with ferric chloride an emerald-green colour.

Protopine $C_{20}H_{19}NO_5$ forms small prisms melting at 202°; it gives no colour with ferric chloride, and dissolves in sulphuric acid containing ferric sulphate with a dark-violet colour.

Papaverine $C_{21}H_{21}NO_4$ crystallizes from alcohol in colourless prisms, dissolving in hot sulphuric acid with a dark-violet colour; on adding water to this solution brown amorphous flakes separate out, dissolving in alkalis with a splendid purple colour.

Nitropapaverine $C_{21}H_{20}(NO_2)NO_4 + H_2O$ is obtained by the action of strong nitric acid on papaverine, and crystallizes in yellowish needles. It is a base forming crystalline salts.

Meconidine $C_{21}H_{23}NO_4$ is an amorphous mass which is soluble in caustic potash. It forms amorphous unstable salts, and dissolves in sulphuric acid with an olive-green colour.

Laudanosine $C_{21}H_{27}NO_4$ is very soluble in ether, and crystallizes from benzene in beautiful white needles melting at 89°. It dissolves in sulphuric acid containing ferric sulphate with a brownish-red colour, which on heating first becomes green and then dark-violet.

Rhœadine $C_{21}H_{21}NO_6$ exists in *Papaver Rhœas*, and also sometimes in opium. It is a tasteless crystalline powder, and has no poisonous properties.

Cryptopine $C_{21}H_{23}NO_5$ crystallizes from alcohol in short, hexagonal prisms, melting at 217°. Its salts taste bitter and cooling like peppermint. In concentrated sulphuric acid it dissolves with a deep-violet colour.

Nitrocryptopine $C_{21}H_{22}(NO_2)NO_5$ is produced by the action of dilute nitric acid crystallizing from alcohol in pale-yellow plates, which are coloured blood-red by concentrated sulphuric acid.

Lanthopine $C_{23}H_{25}NO_4$ is very sparingly soluble in alcohol, and crystallizes from chloroform in white prisms. It dissolves in concentrated sulphuric acid with a pale-violet colour, which turns dark-brown on heating.

Narceine $C_{23}H_{29}NO_0$ is readily soluble in boiling water, and forms colourless crystals; when given in a small dose it produces quiet sleep. Iodine colours its solution blue, like starch-paste.

ALKALOÏDS OCCURRING IN STRYCHNOS-SPECIES.

The seeds of *Strychnos Nux-vomica* and *Strychnos Ignatius* contain two very poisonous bases.

Strychnine $C_{21}H_{22}N_2O_2$.—The St. Ignatius-beans contain about 1·5 per cent. of this base, which, however, is generally obtained from nux vomica. These very tough seeds are softened by boiling them with alcohol, powdered, and exhausted with boiling dilute alcohol. The alcohol is distilled off, and lead acetate added to the residue, which precipitates foreign matters. The filtrate, after being freed from lead, is concentrated, and the alkaloïds precipitated with magnesia. The precipitate, after standing for some days, is collected on a filter, and exhausted with boiling alcohol. On cooling, the greater portion of the strychnine crystallizes out; the mother-liquor is neutralized with nitric acid and concentrated. On leaving it to stand, strychnine nitrate crystallizes out, and is purified by recrystallization.

Strychnine crystallizes in brilliant rhombic prisms, possessing such an intensely bitter taste that it is even perceptible in a solution of one part of the base in one million parts of water. In water it dissolves but sparingly, more readily in dilute alcohol, and very freely in chloroform; in ether and absolute alcohol it is insoluble. It forms soluble and crystallizable salts, having an intensely bitter taste, and being, like the base itself, fearful poisons, producing in a small dose tetanus and death. The antidotes are morphine, atropine, and chloral hydrate.

The least trace of strychnine can be readily identified by moistening it with pure concentrated sulphuric acid, and adding a crystal of potassium dichromate, when a deep-purple colour is produced, changing soon into red and yellow. Another very delicate test is to inject a small quantity of a very dilute solution under the skin of a frog;

tetanic convulsions will soon set in, and, if the dose was not large enough to kill the frog, will last for hours.

Strychnine is a monacid tertiary base; *strychnine-methylammonium iodide* $(N_2(C_{21}H_{22}O_2)CH_3I$ is a crystalline solid, and readily decomposed by treating it with silver oxide and water; the hydroxide has not bitter taste, nor does it, or its salts, act as poison when taken internally, but when injected under the skin it produces paralysis like *curarine* (see below).

On adding a solution of strychnine to alcoholic, yellow ammonium sulphide, a precipitate is formed, consisting of orange-red needles having the composition $C_{21}H_{22}N_2O_2 + H_2S_3$. It is decomposed by dilute sulphuric acid, and *hydrogen trisulphide* H_2S_3 separates out as a colourless oily liquid.

Brucine $C_{23}H_{26}N_2O_4 + 4H_2O$ occurs together with strychnine in the seeds of Strychnos Nux-vomica, and alone in the bark of this tree (*false Angostura-bark*). It is prepared from the mother-liquor of strychnine nitrate, by precipitating it with ammonia, and crystallizing the base from alcohol. It forms colourless prisms, which lose their water of crystallization when exposed to the air.

It is more soluble than strychnine, and has a bitter taste; its poisonous properties are similar to those of strychnine, but it acts less violently. With nitric acid it forms a red solution which becomes yellow on heating, and when now stannous chloride is added the liquid assumes a deep-violet colour.

When heated with sulphuric acid and manganese dioxide, it yields methyl alcohol, and concentrated nitric acid, converts it into methyl nitrate, oxalic acid, and *cacoteline* $C_{20}H_{22}(NO_2)_2N_2O_5$, a weak base, forming yellow crystals.

Brucine is a tertiary base; the salts of brucine-methylammonium act like the corresponding compounds of strychnine, but less energetically.

Curarine $C_{10}H_{15}N$ is the active principle of the South American arrow-poison, which is prepared from the milky juice of different species of strychnos. It forms colourless crystals, having a very bitter taste. When one milligram is injected under the skin of a rabbit, paralysis very soon sets in, and the animal dies.

ALKALOÏDS OCCURRING IN CINCHONA-BARKS.

The barks of different species of *Cinchona*, which are indigenous to the eastern slopes of the Andes, and are also cultivated in India and Java, contain a number of bases in combination with quinic acid. The following have been isolated:—

Quinine . . .	$C_{20}H_{24}N_2O_2$	Cinchonidine .	$C_{20}H_{24}N_2O$
Conquinine . .	$C_{20}H_{24}N_2O_2$	Paytine . . .	$C_{21}H_{24}N_2O_2$
Quinamine . .	$C_{20}H_{26}N_2O_2$	Paricine . . .	—
Cinchonine . .	$C_{20}H_{24}N_2O$		

The most important of these is quinine, which always occurs together with cinchonine. The yellow bark (*Cinchona Calysaya*) contains 2 to 3 per cent. of quinine, and 0·2 to 0·3 of cinchonine; while the pale bark (*Cinchona Condaminea*) contains about 0·8 of quinine, and 2 of cinchonine, and the red bark (*Cinchóna succirubra*), about 2 of quinine and 1 of cinchonine.

Quinine $C_{20}H_{24}N_2O_2 + H_2O$.—For the preparation of this compound the yellow or red bark is chiefly used. It is treated with very dilute hydrochloric acid, and the solution is precipitated with sodium carbonate. The precipitate is washed, and after being dried, exhausted with boiling alcohol. The liquid is neutralized with sulphuric acid, and the alcohol distilled off; from the residual liquid, impure quinine sulphate crystallizes out, which is purified by dissolving it again in alcohol, adding animal charcoal to decolorize the solution, and crystallizing the sulphate by concentrating the liquid.

Ammonia precipitates quinine as a powder, which dissolves in 900 parts of cold water, and is tolerably soluble in ether, and freely in alcohol, crystallizing from these solutions as a powder, and from chloroform in distinct prisms.

Quinine is a tertiary base, and forms several series of salts, those containing one equivalent of an acid are sparingly soluble in water, while those containing more than one equivalent are readily soluble, and form highly fluorescent solutions, the reflected light being of a sky-blue colour. Quinine and its salts have an intensely bitter taste.

Basic Quinine Sulphate $2(C_{20}H_{24}N_2O_2)SO_4H_2 + 8H_2O$ is manufactured on a very large scale, and crystallizes in long brilliant needles, which soon lose some water, and form a very light crystalline powder. It dissolves in 780 parts of cold water, and more readily in alcohol, and in boiling water.

Normal Quinine Sulphate $C_{20}H_{24}N_2O_2.SO_4H_2 + 7H_2O$ is obtained by dissolving the basic salt in dilute sulphuric acid, and forms transparent four-sided prisms, which dissolve in 11 parts of cold water.

Acid Quinine Sulphate $C_{20}H_{24}N_2O_2.2SO_4H_2 + 7H_2O$ forms soft white prisms, and is freely soluble in water; its solution exhibits a splendid fluorescence.

When the basic sulphate is dissolved in acetic acid, and a solution of iodine is added, large thin plates separate out, consisting of $C_{20}H_{24}N_2O_2.SO_4H_2I_2$; they appear almost colourless by transmitted light, but show by reflection a brilliant emerald colour. This beautiful compound possesses the optical properties of turmaline, and is used for optical experiments, under the name of *Herapathite*.

Basic Quinine Hydrochloride $C_{20}H_{24}N_2O_2.ClH + 1\frac{1}{2}H_2O$ crystallizes in silky needles.

Normal Quinine Hydrochloride $C_{20}H_{24}N_2O_2(ClH)_2$ does not crystallize well, and is decomposed by water into the basic salt and free acid. By adding platinic chloride to its solution, the double salt $C_{20}H_{24}N_2O_2(ClH)_2 + PtCl_4 + H_2O$ is obtained as a pale-yellow precipitate, which, on standing, changes into orange-red crystals.

The solutions of quinine, and its salts, turn the plane of polarization strongly to the left. Its salts dissolve in chlorine-water, forming a colourless solution, which, on adding ammonia, assumes a deep-emerald colour. If first potassium ferrocyanide be added, and then ammonia, the liquid becomes deep-red.

Quinine and its salts are powerful tonics, and most useful in intermittent fevers.

Conquinine, or *Quinidine* $C_{20}H_{24}N_2O_2 + H_2O$, is contained in different barks, chiefly in that of *Cinchona pitayensis*, and the yellow barks from India. It is conveniently prepared from the mother-liquors of quinine sulphate; on evaporating them, a resinous mass is left behind, called *quinoïdine*, which is exhausted with ether, and after the ether has been distilled off, the residual solution is dissolved in dilute sulphuric acid. The hot liquid is neutralized with ammonia, and precipitated with a solution of Rochelle-salt. The precipitate containing the tartrates of conquinine, and cinchonidine is dissolved in a large quantity of water, and the solution precipitated with potassium iodide. The conquinine hydriodide thus obtained is decomposed with ammonia, and the base crystallized from alcohol. It forms large prisms, which dissolve but sparingly in water, and give with chlorine and ammonia the quinine reactions. It is as powerful a tonic as quinine, from which it differs by having a strong right-handed rotatory power.

Quinicine $C_{20}H_{24}N_2O_2$ is produced when quinine or conquinine is heated with a little dilute sulphuric acid to 130°. It is a resinous mass, but forms crystallizable salts, and has a feeble right-handed rotation. It appears to exist also in the barks, and in quinoidine.

Quinamine $C_{20}H_{26}N_2O_2$ is found, but only in a very small quantity, in the red bark from India. It forms long, white, light prisms, and is very sparingly soluble in cold water, a little more readily in hot water, and freely in alcohol, and possesses right-handed rotatory power.

Cinchonine $C_{20}H_{24}N_2O$.—This base is readily separated from quinine, as it is almost insoluble in water, and ether, and only sparingly soluble in alcohol, one part requiring 30 parts of boiling alcohol. It crystallizes in brilliant needles, and forms salts resembling those of quinine, but being more soluble in water and alcohol. It turns the plane of polarization strongly to the right, and yields with chlorine-water and ammonia a yellowish precipitate. It is not used in medicine, as it has only feeble tonic properties.

Oxycinchonine $C_{22}H_{23}(OH)N_2O$.—This isomeride of quinine is formed by treating cinchonine with cold bromine, and acting on the monobromocinchonine thus formed with caustic potash; it is a crystalline substance, which is insoluble in ether and water.

Cinchonidine $C_{20}H_{24}N_2O$ occurs in different barks, and in quinoïdine, and differs from cinchonine chiefly by its strong left-handed rotatory power.

Cinchonicine $C_{20}H_{24}N_2O$ is obtained by heating its isomerides with a little sulphuric acid; the base as well as its salts are very similar in its properties to quinicine, and its salts.

Paytine $C_{21}H_{24}N_2O_2 + H_2O$ has been found in a white bark from Payta; it forms white needles or prisms, and possesses left-handed polarization. By adding bleaching-powder to its acid solution, it colours first red, and then blue, but the colour very soon disappears.

Paricine occurs in the red barks from India, and in other barks. It is yellowish-white powder, which readily dissolves in ether and alcohol; its composition is not known.

ALKALOÏDS OCCURRING IN CHELIDONIUM MAJUS.

The common celandine contain two bases.

Chelerythrine $C_{19}H_{17}NO_4$ exists also in the root of *Sanguinaria canadensis* and in *Glauceum luteum*. It crystallizes from alcohol in warty masses, possessing a very acrid taste; it is poisonous, and its dust produces violent sneezing. Its salts have a red colour, and give with water an orange-red solution.

Chelidonine $C_{19}H_{17}N_3O_3 + H_2O$ crystallizes from alcohol in glistening plates, having a bitter taste; it is not poisonous, and forms colourless salts.

ALKALOÏDS OCCURRING IN VERATRUM.

Veratrine $C_{32}H_{52}N_2O_8$ exists in the seeds of *Veratrum Sabadilla* and in the root of *Veratrum album*. It is almost insoluble in water, but dissolves in ether, and alcohol, and crystallizes in white prisms, melting at 115°, and solidifying again to a resinous mass. Veratrin is a most violent poison, and its dust produces violent sneezing. With concentrated sulphuric acid it forms a yellow solution which gradually becomes blood-red.

Jervine $C_{30}H_{46}N_2O_3$ occurs only in *Veratrum album*, and forms colourless prisms; its salts are much less soluble than those of *veratrine*.

ALKALOÏDS OCCURRING IN BERBERIS VULGARIS.

Berberine $C_{20}H_{17}NO_4 + 5H_2O$ exists in the root of this shrub, and also in the roots of *Cocculus palmatus* and *Hydrastis canadensis*. It is soluble in water and alcohol, and crystallizes in yellow needles, possessing, as well as its yellow salts, an intensely bitter taste.

By the action of zinc and dilute sulphuric acid, it is converted into *hydroberberine* $C_{20}H_{21}NO_4$, which separates from an alcoholic solution in very brilliant, colourless crystals.

Oxyacanthine occurs in the root of berberis, and crystallizes from alcohol in colourless prisms, which, when exposed to the sunshine, assume a yellow tint; its composition is not known.

BEBEERINE $C_{10}H_{21}NO_3$.

This base is found in the bark of the bebeero, or greenhart-tree of British Guiana (*Nectandra Rodiei*) and of *Geoffroya jamaicensis*, and in the trunk and roots of *Cissampelos Pareira*, and in *Buxus sempervivens.* It is a colourless amorphous powder, and insoluble in water, but dissolves in alcohol; its solution has a very bitter taste, and an alkaline reaction. *Bebeerine sulphate* $2(C_{10}H_{21}NO_3)SO_4H_2$ is sometimes used as a substitute for quinine.

PIPERINE $N\left\{\begin{matrix}C_5H_{10}\\C_{12}H_9O_3\end{matrix}\right.$.

This weak base exists in different kinds of pepper, and is prepared by exhausting white pepper with alcohol and evaporating the solution; the residue is dissolved in alcoholic potash, and the impure piperine, which, on concentrating this solution, crystallizes out, is purified by recrystallization from alcohol.

Piperine forms colourless, tasteless, and inodorous prisms; its alcoholic solution possesses a sharp peppery taste, and a neutral reaction.

On boiling with alcoholic potash it is resolved into *piperidine* $C_5H_{11}N$, and *piperic acid* $C_{12}H_{10}O_4$.

Piperidine $N\left\{\begin{matrix}C_5H_{10}\\H\end{matrix}\right.$ is a colourless liquid, which is soluble in water, and boils at 106°; it has a pungent and caustic taste, and an ammoniacal and peppery smell. It is a powerful base, forming crystallizable salts. When treated with benzoyl chloride it is converted into *benzoyl-piperidine* $N\left\{\begin{matrix}C_5H_{10}\\C_7H_5O\end{matrix}\right.$ which is a compound corresponding to piperine.

Piperic Acid $C_{12}H_{10}O_4$ is a monobasic acid, crystallizing from hot alcohol in long needles, melting at 210°. Nascent hydrogen converts it into *hydropiperic acid* $C_{12}H_{12}O_4$, which consists of needles, melting at 64°.

By adding potassium permanganate to a solution of potassium piperate, *piperonaldehyde* is formed:—

$$C_{12}H_{10}O_4 + 4O_2 = C_8H_6O_3 + C_2H_2O_4 + 2CO_2 + H_2O$$

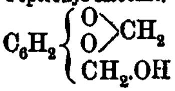
Piperonaldehyde $C_8H_6O_3$ crystallizes from water in transparent, brilliant prisms, melting at 263°, and smelling like cumarin; it combines like other aldehydes with the acid sulphites of the alkali-metals.

Piperonyl Alcohol $C_8H_8O_3$ is produced by the action of sodium-amalgam and water on the aldehyde, and forms colourless crystals, melting at 51°.

Piperonic Acid $C_8H_6O_4$ is produced by the further action of potassium permanganate on the aldehyde. It crystallizes in long needles, melting at 228°. When it is heated with dilute hydrochloric acid to 170°, it is resolved into finely divided carbon, and protocatechuic acid. Phosphorus pentachloride converts it into *dichloropiperonyl chloride* $C_7H_3Cl_2O_2.COCl$, which yields with water dichloropiperonic acid; and the latter, when boiled with water, is resolved into carbon dioxide, hydrochloric acid, and protocatechuic acid.

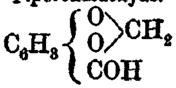
On the other hand, by heating protocatechuic acid with potash, and methene di-iodide (di-iodomethane), it is converted into piperonic acid. These reactions prove that the piperonyl compounds are constituted as follows :—

Piperonyl Alcohol.



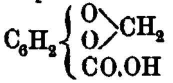
$$C_6H_2\left\{\begin{array}{l} O \\ O \end{array}\right\rangle CH_2 \\ \quad CH_2.OH$$

Piperonaldehyde.



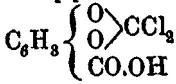
$$C_6H_3\left\{\begin{array}{l} O\rangle CH_2 \\ O \\ COH \end{array}\right.$$

Piperonic Acid.



$$C_6H_2\left\{\begin{array}{l} O\rangle CH_2 \\ O \\ CO.OH \end{array}\right.$$

Dichloropiperonic Acid.



$$C_6H_3\left\{\begin{array}{l} O\rangle CCl_2 \\ O \\ CO.OH \end{array}\right.$$

SINAPINE $C_{16}H_{23}NO_5$.

This base exists as sulphocyanate in the seed of white mustard. To obtain this salt the crushed seed, which has been freed from the fatty oil by pressing, is exhausted with alcohol; it is a light crystalline powder, consisting of needles. The free sinapine is not known; on boiling one of its salts with water, the base is resolved into *choline* and bibasic *sinapic acid* $C_{11}H_{12}O_5$, crystallizing from hot water in colourless prisms. This decomposition is explained by the following equation :—

$$N\left\{\begin{array}{l} C_2H_4O.CO \\ (CH_3)_3O.CO \end{array}\right\} C_9H_{10}O + 2H_2O = \overset{\text{Choline.}}{N\left\{\begin{array}{l} C_2H_4.OH \\ (CH_3)_3OH \end{array}\right.} +$$

$$\overset{\text{Sinapic Acid.}}{\left.\begin{array}{l} HO.CO \\ HO.CO \end{array}\right\} C_9H_{10}O}$$

ATROPINE $C_{17}H_{23}NO_3$.

This powerful poison exists in the deadly nightshade (*Atropa Belladonna*), and in the thornapple (*Datura Stramonium*). To prepare it the expressed juice of the flowering belladonna is heated to 90°, filtered, and the liquid, after addition of potash, shaken with chloroform. The impure atropine, which is left behind by distilling the chloroform off, is crystallized from alcohol. It forms prisms, having a nauseous bitter and burning taste, and imparting a dry sensation to the mouth with constriction of the throat. In a very small dose it produces headache, and dilates the pupil powerfully.

When heated with baryta-water it is resolved into *tropic acid* (page 394), and *tropine* $C_8H_{15}NO$, a base crystallizing in needles:—

$$N\left\{\begin{array}{l}C_8H_{14}O\\ CO(C_2H_3OH)C_6H_5\end{array}\right. + H_2O = N\left\{\begin{array}{l}C_8H_{14}O\\ H\end{array}\right. +$$
$$HO.CO(C_2H_3.OH)C_6H_5$$

COCAÏNE $C_{17}H_{21}NO_4$.

This compound is the active principle of the coca-leaves (*Erythroxylon Coca*), which are used as a stimulant in Peru. It crystallizes from alcohol in monoclinic prisms. When heated with hydrochloric acid, it is resolved into methyl alcohol, benzoic acid, and *ecgonine* $C_9H_{15}NO_3$ a base crystallizing from water in glistening prisms:—

$$\left.\begin{array}{r}CH_3\\ C_9H_{13}O_2\\ C_6H_5.CO\end{array}\right\}\begin{array}{l}O\\ N\end{array} + 2H_2O = CH_3.OH + C_9H_{15}NO_3 + C_6H_5.CO.OH$$

PHYSOSTIGMINE OR ESERINE $C_{15}H_{21}N_3O_2$.

This base is found in the Calabar-bean (*Physostigma venosum*). It is a crystalline body, which is sparingly soluble in water, and freely in alcohol, and has a strongly alkaline reaction. It is a violent poison, and produces a powerful contraction of the pupil.

HYOSCYAMINE $C_{15}H_{23}NO_3$.

The poisonous principle of the henbane (*Hyoscyamus niger*) forms colourless thin prisms, which in the pure state are odourless, but when impure possess a nauseous smell. It dilates the pupil like atropine.

By boiling it with baryta-water it is resolved into *hyoscinic acid* $C_0H_{10}O_3$, and a powerful crystalline base called *hyoscine* $C_6H_{13}N$.

ACONITINE $C_{27}H_{30}NO_{10}$.

This most violent poison exists in the purple monkshood (*Aconitum Napellus*); it forms rhombic plates, having a sharp and pungent taste.

COLCHICINE $C_{17}H_{10}NO_5$

is a weak base occurring in *Colchicum autumnale*, and forms an amorphous powder, possessing a very acrid taste, and producing, in a small dose, vomiting and diarrhœa. On heating it with dilute acids, it is converted into the isomeric *colchiceine*, which is a weak acid, crystallizing in needles.

EMETINE $C_{30}H_{44}N_2O_8$.

The active principle of *Ipecacuanha* is a light greyish powder, having a bitter taste, and producing, in a small dose, speedy vomiting.

HARMALINE $C_{13}H_{14}N_2O$.

This body is extracted by acetic acid from the seeds of *Peganum Harmala*—a plant indigenous to the steppes of Southern Russia—and which are used in dyeing. Harmaline crystallizes in rhombic octahedrons, and forms salts having a yellow colour.

Harmine $C_{13}H_{12}N_2O$ is obtained by oxidizing harmaline and is also contained in the seeds; it is a base, and forms colourless prisms.

SOLANINE $C_{13}H_{71}NO_{16}$.

This compound is a weak base which is found in different species of solanum, and chiefly in *Solanum nigrum*, and in the shoots of potatoes which have been kept in a cellar during winter. It is poisonous, and crystallizes in silky needles.

Solanidine $C_{25}H_{41}NO$.—Solanine is a glucoside, and resolved by boiling dilute hydrochloric acid into glucose and solanidine:—

$$C_{43}H_{71}NO_{16} + 3H_2O = 3C_6H_{12}O_6 + C_{25}H_{41}NO$$

Solanidine is a strong base, and crystallizes from alcohol in long silky needles.

Besides these alkaloïds there exists a large number of others, which, however, have been but imperfectly studied, and are not of much importance. Of these the following may be mentioned:—

Corydaline $C_{18}H_{19}NO_4$ occurs in the roots of different species of *Corydalis*, and forms colourless crystals, possessing a bitter taste and strongly alkaline reaction.

Cytisine $C_{24}H_{27}N_3O$ is found in the seeds of *Cytisus Laburnum*, and forms colourless crystals having a caustic and bitter taste, and an alkaline reaction.

Delphinine $C_{24}H_{35}NO_2$ is a yellow powder possessing an unbearable acrid taste, and occurring in the seeds of *Delphinium Staphisagria.*

Lycine $C_5H_{17}NO_2$ is found in the leaves of *Lycium barbarum*, and forms a crystalline deliquescent mass, having a neutral reaction and a pungent taste.

Menispermine is a base existing in the seeds of *Menispermum Cocculus*; it forms colourless prisms, and appears not to be poisonous; the poisonous principle of the seeds being picrotoxin (page 487).

COLOURING AND BITTER PRINCIPLES.

There exist, chiefly in the vegetable kingdom, a large number of definite compounds which are neither glucosides nor alkaloïds, and are distinguished by characteristic colours, or a bitter or sharp taste. The following are the more important ones of this not well defined group.

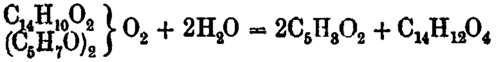
Aloïn $C_{17}H_{18}O_7$ is the active principle of aloes, from which it may be extracted by cold water. On evaporating the solution *in vacuo*, and leaving it to stand, small pale yellow needles are obtained, which are not freely soluble in water and alcohol. It has a sweetish-bitter taste, and a nauseous smell; when heated it melts, and solidifies on cooling to a brown resinous mass.

Cold fuming nitric acid converts it into oxalic acid, picric acid, chrysammic acid, and *aloetic acid* $C_{14}H_4(NO_2)_4O_2$, a yellowish-red crystalline powder, forming red salts, and yielding chrysammic acid by protracted boiling with nitric acid.

Athamanthin $C_{24}H_{30}O_7$ is a constituent of the unripe seeds and root of *Athamanta Oreoselinum*, and consists of colourless prisms, possessing a rancid smell, and a bitter and acrid taste. It forms definite compounds with sulphur dioxide and hydrochloric acid; the latter is resolved by the action of heat into *valerianic* acid and *oreoselon* $C_{14}H_{10}O_3$, a crystalline body which is soluble in alcohol and alkalis. Boiling hydrochloric acid converts it into *oreoselin* $C_{14}H_{12}O_4$, which is also soluble in alkalis and alcohol, and crystallizes in slender needles.

By treating athamantin with nitric acid it yields a yellow powder of *trinitro-athamantin* $C_{24}H_{27}(NO_2)_3O_7$, which is insoluble in water.

Peucedanin $C_{24}H_{24}O_6$ exists in the roots of *Peucedanum officinale* and *Imperatorium Obstruthium*, and crystallizes from alcohol in brilliant prisms. On boiling with alcoholic potash it is resolved into *angelic acid* and *oreoselin*.



$$\left.\begin{matrix} C_{14}H_{10}O_2 \\ (C_5H_7O)_2 \end{matrix}\right\} O_2 + 2H_2O = 2C_5H_8O_2 + C_{14}H_{12}O_4$$

Concentrated nitric acid converts it into *dinitropeucedanin* $C_{24}H_{22}(NO_2)_2O_6$, which forms colourless flexible plates.

Laserpitin $C_{24}H_{30}O_7$ is contained in *Laserpitium millefolium*, and is insoluble in water, but dissolves in alcohol; it forms brilliant prisms, melting at 114°, and subliming without decomposition. By the action of alcoholic potash it is resolved into angelic acid and amorphous *lascrol* $C_{14}H_{22}O_4$.

Cantharidin $C_5H_6O_2$ is the active principle of the Spanish fly, from which it can be extracted by ether. It crystallizes in colourless, tasteless and inodorous plates, melting at 250°, and subliming without decomposition. It dissolves in boiling potash, forming the salt $C_5H_7KO_3$, which is decomposed by acids with the formation of cantharidin and water.

Carotin $C_{18}H_{24}O$ is found deposited as small crystals in the cells of the carrot, and crystallizes from alcohol in small reddish-brown crystals possessing a fragrant odour.

Hydrocarotin $C_{18}H_{30}O$ is also found in carrots; it crystallizes from ether in large, colourless, rhombic plates.

Chlorophyll is the name given to the green colouring matter of leaves; it is soluble in alcohol, ether and hydrochloric acid. Its composition is not known; it contains no nitrogen, but iron appears to be an essential constituent.

Colombin $C_{21}H_{22}O_7$ exists together with berberin in calumba-root, and forms colourless crystals, having a bitter taste.

Curcumin $C_{10}H_{10}O_3$ is the colouring matter of turmeric; it is insoluble in cold water, and dissolves sparingly in boiling water, freely in alcohol; the solution exhibits a green fluorescence. It forms brilliant yellow crystals; nitric acid oxidises it to oxalic acid.

Rosocyanin.—When turmeric paper is moistened with solution of boric acid, it assumes, on drying, an orange colour, which by alkalis is changed into a pure blue, turning soon into grey. This reaction is caused by the formation of a peculiar compound of unknown composition, called rosocyanin. It is prepared by boiling an alcoholic solution of curcumin with boric acid and strong sulphuric acid. Rosocyanin forms slender needles, having a green-metallic lustre, and dissolving in alcohol with a splendid red colour, which on adding a drop of soda changes into a deep-blue, and when exposed to the air turns grey. Lime and baryta-water give with the alcoholic solution fine blue precipitates.

Helenin $C_{21}H_{28}O_8$ occurs in the root of *Inula Helenium*, and crystallizes in colourless four-sided prisms, which are soluble in alcohol. When heated with phosphorus pentoxide it is resolved into water, carbon dioxide and liquid *Helenene* $C_{19}H_{26}$.

Ivaïn $C_{24}H_{42}O_3$ is found in Iva (Achillea moschata) a plant growing in the High-Alps. It is a yellow semifluid resinous mass, having an intensely bitter taste.

Ivaol $C_{24}H_{40}O_2$ is the volatile oil of Iva, and possesses a very agreeable aromatic odour, and bitter and warming taste. Besides these compounds Iva contains *Moschatin* $C_{21}H_{27}NO_7$ and

Achillein $C_{20}H_{38}N_2O_{15}$, which is also found in *Achillea millefolium* and forms an amorphous powder. When boiled with dilute acids it yields ammonia, a volatile body having a fragrant smell, and *achilletin* $C_{11}H_{17}NO_4$, a brown substance having an aromatic but not bitter taste.

Picrotoxin $C_{12}H_{14}O_5$ is the poisonous principle contained in the seeds of *Menispermus Cocculus* and prepared by exhausting them with alcohol, and crystallizing the impure picrotoxin from hot water. It forms tufts of colourless needles, having an intensely bitter taste.

Quassiin $C_{10}H_{12}O_3$ is contained in the quassia-wood (*Picraena excelsa*) from Jamaica, and forms thin colourless crystals, which are sparingly soluble in water, freely in alcohol, and possess a very bitter taste.

Santonin $C_{15}H_{18}O_3$ occurs in *Semen-contra* or worm-seed, which consists of the unexpanded flower-heads of *Artemisia Santonica*. To prepare it, worm-seed is boiled with milk of lime, and the solution precipitated with hydrochloric acid. It crystallizes from alcohol in colourless, flat, six-sided prisms, having a faint bitter taste; when exposed to sunshine the crystals become yellow. Santonin is a weak acid; the sodium salt $2(C_{15}H_{17}NaO_3) + 9H_2O$ crystallizes in colourless, translucent plates, and is decomposed by boiling water. Santonin is used as an anthelminic.

Turacin is the red colouring matter contained in feathers of the wing of the *Turaco* or plantain-eater, from which it may be extracted by dilute potash. Its composition is not known, but it differs from all other red colouring matters by containing 5·9 per cent. of copper; the presence of this metal can easily be shown by the green colour, which the feathers impart to the colourless gas-flame; the green feathers of this bird do not contain copper.

COMPOUNDS CONTAINED IN BILE AND OTHER SECRETIONS.

Bile contains a number of peculiar compounds, some of them occuring also in other parts of the animal organism.

Glycocholic Acid $C_{26}H_{43}NO_6$ is conveniently prepared by evaporating fresh ox-bile on a water bath nearly to dryness, exhausting the residue with alcohol of 90 per cent., evaporating the solution, and heating with milk of lime to precipitate the colouring matter. On adding dilute sulphuric acid to the cold filtrate and leaving it to stand, glycocholic acid crystallizes out, which is purified by pressing it between filter-paper, dissolving the residue in lime-water, and precipitating the acid with dilute sulphuric acid.

It crystallizes in white needles, having a bitterish sweet taste. In concentrated sulphuric acid it dissolves, forming a colourless liquid, which on adding a solution of sugar becomes violet.

When glycocholic acid is boiled with dilute acids, or alkalis, it is resolved into glycocoll or amidacetic acid, and *cholic acid* $C_{24}H_{40}O_5$, which crystallizes from alcohol in brilliant octahedrons. By protracted boiling with acids it is converted into *dyslysin* $C_{24}H_{36}O_3$, an amorphous, neutral substance, which is reconverted into cholic acid by the action of caustic potash.

Taurocholic Acid $C_{26}H_{45}NSO_7$ is prepared by dissolving fresh ox-bile in water and precipitating glycocholic acid, colouring matters and other substances with lead acetate. To the filtrate a little basic lead acetate is added, which removes the remainder of the glycocholic acid, and then the clear solution is precipitated by adding some more lead acetate and ammonia. The lead taurocholate is decomposed by hydrogen sulphide, and thus the free acid is obtained, crystallizing in fine silky needles. By heating it with water it is resolved into cholic acid and taurine (page 192).

Human bile contains principally glycocholic acid, and only a small quantity of taurocholic acid, which occurs alone in the bile of the dog.

Hyoglycocholic Acid $C_{27}H_{43}NO_5$ and *hyotaurocholic acid* $C_{27}H_{45}NSO_6$ exist in the bile of the pig and have been resolved into gycocoll, or taurine and *hyocholic acid* $C_{25}H_{40}O_4$, a compound resembling cholic acid.

Chenotaurocholic Acid $C_{29}H_{49}NSO_6$ is homologous with hyotaurocholic acid, and occurs in the bile of the goose; it yields, as products of decomposition, taurine and *chenocholic acid* $C_{27}H_{44}O_4$.

Lithofellic Acid $C_{20}H_{36}O_4$ forms the chief constituent of the once celebrated "oriental bezoar-stones," which are said to be biliary calculi from a species of antelope. It crystallizes from alcohol in small transparent six-sided prisms, which with sulphur acid and sugar give the same reaction as glycocholic acid.

Cholesterin $C_{26}H_{44}O + H_2O$ is found in the bile, the brain and nerves, in blood and the yolk of eggs, and forms the chief constituent of biliary calculi; it has also been found in plants. From alcohol it crystallizes in small, brilliant plates, and from ether-alcohol in beautiful large plates, which are tasteless, and colourless, and melt at 145°, and sublime when more strongly heated.

Cholesterin is a monad alcohol, and apparently homologous with cinnyl alcohol.

Cholesteryl Chloride $C_{26}H_{43}Cl$ is produced by heating cholesterin with strong hydrochloric acid and crystallizes in colourless needles.

Cholesterylamine $C_{26}H_{43}.NH_2$ is obtained by heating the chloride with alcoholic ammonia. It crystallizes in small iridescent plates, melting at 104°, and exhibiting in the liquid state a fine bluish violet fluorescence.

Cholesteryl Acetate $C_{20}H_{43}O.C_2H_3O$ is formed by heating cholesterin with acetyl chloride, and crystallizes from hot alcohol in small needles, melting at 92°.

Cholesteryl Benzoate $C_{20}H_{43}O.C_7H_5O$ is produced by heating cholesterine with benzoic acid in sealed tubes to 200°. It crystallizes from ether in small, thick, rectangular plates, melting at 125°.

Oxycholic Acid $C_{24}H_{40}O_6$ is obtained by oxidizing cholesterin with a dilute solution of chromic acid. It is an amorphous mass, having a bitterish-sweet taste.

Isocholesterin $C_{20}H_{44}O$ is found together with cholesterin and fatty acids in suint. It crystallizes from ether in slender, transparent needles, melting at 137°.

Isocholesteryl Benzoate $C_{20}H_{43}O.C_7H_5O$ crystallizes from acetone in tufts of brilliant needles, and from ether in microscopic needles.

Bilirubin $C_{16}H_{18}N_2O_3$ exists in small quantity in the bile of different animals, and in larger quantity combined with calcium in certain biliary calculi, and is best obtained from those of the ox. It is insoluble in water, sparingly soluble in alcohol and ether, freely in chloroform, and forms dark-red crystals. In alkalis it dissolves with a dark-orange colour; the salts of other metals produce dark-brown precipitates in this solution.

Biliverdin $C_{16}H_{20}N_2O_5$.—When an alkaline solution of bilirubin is exposed to the air it turns green, and on addition of an acid a green precipitate is formed, crystallizing from glacial acetic acid in green rhombic plates.

Hydrobilirubin or *Urobilin* $C_{32}H_{40}N_4O_7$ is produced by the action of sodium-amalgam, and water on bilirubin, and biliverdin, and exists also in urine, chiefly in the dark-coloured one of fever-patients. It dissolves in alcohol and chloroform with a yellowish-red colour, and in alkalis with a brown colour. By adding a little zinc sulphate to its ammoniacal solution the liquid assumes a red colour, and exhibits a green fluorescence.

Bilifuscin $C_{16}H_{20}N_2O_4$ is an almost black, glistening, brittle mass, dissolving in alkalis and alcohol with a brown colour; it is found in small quantity in biliary calculi.

Biliprasin $C_{16}H_{22}N_2O_6$ occurs in biliary calculi, and in the ox-bile. It is a dark-green powder, insoluble in water, and dissolving in alcohol with a green colour, and in alkalis with a brown colour.

When nitric acid containing a little nitrous acid is added to an alkaline solution of any of these colouring matters of bile, the liquid first assumes a *yellow colour, changing successively into* green, blue, violet, red, and finally again into yellow.

Bilihumin is a dark brown substance existing in all biliary calculi, and which is also the final product produced by exposing an alkaline solution of the other colouring matters of bile to the air.

Cystine $C_3H_7NSO_2$ occurs in the form of calculi or sediment in the bladder. On dissolving it in ammonia, and allowing the solution to evaporate, it is obtained in small, colourless, six-sided plates. On heating it with soda-solution it yields sodium sulphide, and when treated with zinc and hydrochloric acid it gives off hydrogen sulphide. It has probably the following constitution:—$C_2H_3(SH)(NH_2)CO_2H$.

Kynurenic Acid $C_{20}H_{14}N_2O_6$ exists in the urine of the dog, and forms, in the pure state, silver-white glistening needles containing 2 molecules of water; it is insoluble in water, but dissolves in concentrated acids. *Barium Kynurenate* $C_{20}H_{12}BaN_2O_6 + 3H_2O$ is sparingly soluble in water and crystallizes in glistening compact needles.

When kynurenic acid is heated to 265° it melts, giving off carbon dioxide, and being converted into *Kynurine* $C_{18}H_{14}N_2O_2$, crystallizing from warm water in beautiful transparent prisms, melting at 210°. The hydrochloride $C_{18}H_{14}N_2O_2(ClH)_2 + 2H_2O$ forms colourless needles, and yields, with platinic chloride, the compound $C_{18}H_{14}N_2O_2(ClH)_2 + PtCl_4$, existing in beautiful crystals.

Lithuric Acid $C_{15}H_{19}NO_9$.—A peculiar kind of calculi, which are *voided with the urine by oxen fed on the stalks of* Indian *corn in* Toskana, consist of the magnesium salt of this acid $(C_{15}H_{18}NO_9)_2Mg$; it crystallizes from boiling water in small monoclinic, transparent prisms, which on heating decompose, giving off the smell of burnt sugar. The free acid crystallizes from hot water in fine, silky, white needles, melting at 205°.

Excretin $C_{20}H_{36}O$ is contained in human fæces, and crystallizes from hot alcohol in small needles. By the action of bromine it is converted into *dibromexcretin* $C_{20}H_{34}Br_2O$, crystallizing from ether-alcohol in hard, globular masses.

ALBUMINOÏDS OR PROTEIDS.

These important compounds form the chief parts of the solid constituents of blood, muscles, glands, and other organs, and occur also in plants, principally in the seeds. Their constitution is completely hidden in darkness; from the results of their ultimate analysis no formula can be calculated, on account of their high molecular weight, which, however, is not known, as they do not form definite compounds with other bodies, and are neither volatile nor crystalline. It is not even known whether some of them are pure compounds or only mixtures. They have all a very similar composition, and contain in 100 parts:—

52—54	parts of	Carbon
7—7·3	„	Hydrogen
13—16	„	Nitrogen
21—26	„	Oxygen
1—1·6	„	Sulphur

They also always contain a small quantity of calcium phosphate.

Most proteids exist in a soluble and an insoluble modification. An aqueous solution of the soluble bodies dries up to a gum-like mass, and is precipitated by different agents, the insoluble modification separating out as amorphous white flakes, or curds.

They all dissolve in glacial acetic acid, in a strong solution of phosphoric acid, in concentrated hydrochloric acid, and in alkalis. When the acetic acid solution is diluted with much water it yields precipitates with potassium ferrocyanide, ferricyanide and platinocyanide. On boiling them with hydrochloride acid in contact with the air, the solution assumes a blue colour, changing gradually into violet and brown. When their alkaline solution is boiled, a part of the sulphur is eliminated in the form of an alkaline sulphide. On heating a proteid with a solution of mercurous nitrate containing nitrous acid, it assumes a fine red colour, and a similar colour is produced by the joint action of a solution of sugar and sulphuric acid.

When exposed to the air in the moist state, they rapidly undergo putrefaction, the products consisting of *ammonia, ammonium sulphide, carbon dioxide, volatile fatty acids, lactic acid, amines, leucine* and *tyrosine.*

The two latter bodies are also produced by boiling a proteid with dilute sulphuric acid.

Chromic acid-solution oxidizes them to *fatty aldehydes, acids* and *nitriles* and *benzaldehyde* and *benzoic acid.*

On heating them with water and bromine under pressure they are resolved into *carbon dioxide, bromoform, bromacetic acid, oxalic acid,* *aspartic acid*, *leucine*, *leucimide*, *bromanil*, and *amidotribromobenzoic acid*.

When heated with hydrochloric acid and stannous chloride, they undergo a very simple decomposition, being resolved into *ammonia*, *aspartic acid*, *glutamic acid*, *leucine* and *tyrosine*.

Serum-Albumin exists in the blood of vertebrate animals, in chyle and lymph, &c., and in small quantity also in milk. In diseases of the kidneys it appears in considerable quantity in urine.

It is prepared by diluting blood-serum with a little water, and adding carefully acetic acid, to precipitate other proteids. The filtrate is evaporated at a temperature not exceeding 40°, and thus an amorphous mass is obtained, giving with cold water a clear solution.

When a solution of albumin is heated to 72° it coagulates to a compact mass. The presence of acids or salts raises the temperature of coagulation, whilst alkalis lower it. On adding hydrochloric acid to a solution of albumin, a precipitate is formed which dissolves in an excess of the acid.

Egg-Albumin is contained in the white of the egg, and differs from serum-albumin by being almost insoluble in nitric acid, and being gradually precipitated when its solution is shaken with ether. It is also precipitated by hydrochloric acid, but dissolves only with difficulty in an excess.

The two albumins possess right-handed rotatory power; that of egg-albumin being less powerful than that of the other.

Vegetable Albumin exists in almost every vegetable juice, and coagulates when its solution is heated; it has not been obtained pure, and is therefore only imperfectly known.

Casein is found in milk and the yolk of eggs, and obtained in a pure state by adding dilute sulphuric acid to milk, from which the cream has been removed, and digesting the curdy precipitate with water and lead carbonate. The solution thus formed is treated with hydrogen sulphide, and the filtrate evaporated at a low temperature.

Casein is insoluble in pure water, but dissolves if a trace of an acid or alkali be present. This solution is precipitated by acids, a compound of casein with the acid being formed. A solution of casein is also precipitated by adding some "rennet" to it, and heating to about 53°, but not by heat alone.

Vegetable Casein or *Legumin* exists in many seeds such as peas, beans, vetches, &c., from which it is obtained by softening them with warm water, and triturating them into a pulp, which is pressed through a sieve. On standing, the liquid deposits starch; the clear solution is then decanted and precipitated with acetic acid. Legumin has great resemblance with milk-casein.

Conglutin is a proteid existing in almonds and lupine-seeds. It is a white powder, which is sparingly soluble in water, and freely in dilute alkalis and in acetic acid. Acids precipitate it from the alkaline solution as a very adhesive mass, drying up to a glassy substance. It is the best material for the preparation of *glutamic acid* (see page 233).

Blood-Fibrin is dissolved in the blood, but coagulates as soon as the blood leaves the living organism, and forms, together with the red blood-globules, the blood-coagulum. But if blood be run from the veins into a concentrated solution of glauber-salt, the fibrin remains in solution, from which, after filtration, it is precipitated by adding common salt.

Muscle-Fibrin or *Myosin*.—To obtain this body, finely chopped meat is exhausted with cold water, and the residue triturated with a solution containing not more than 10 per cent. of common salt. The mucilagenous solution thus obtained is precipitated by adding more salt, myosin being only soluble in a dilute solution of salt, but neither in a concentrated one nor in pure water.

Globulin is contained in blood-serum, and obtained as a granular precipitate by diluting the serum with ten parts of water, and passing a rapid current of carbon dioxide through the solution. It dissolves in very dilute salt-solutions, and in water containing a trace of an acid or alkali, but becomes insoluble when heated with water to 70°.

Vitellin occurs in the yolk of eggs, and is obtained by treating the yolk with ether to remove fats and the colouring matter; it is a white granular powder, which is soluble in salt solutions. It has great resemblance with myosin, from which it differs by not being precipitated by saturating the solution with salt.

Syntonin is produced by the action of weak hydrochloric acid on myosin or that of strong acid on any other proteid. When the solution thus formed is diluted with water, syntonin is precipitated in combination with the acid. When this compound is decomposed by a dilute solution of sodium carbonate, syntonin goes in solution. It is insoluble in water, but dissolves in acids and in alkaline carbonates.

Vegetable Fibrin.—When wheaten flour is made into a paste with water, and this is tied up into a cloth and washed with water as long as starch passes through, an adhesive, elastic substance is left behind, which is called *gluten*, and consists of a mixture of vegetable fibrin and gliadin. They are separated by dissolving the gliadin in alcohol and treating the residual fibrin with ether to remove fat. Vegetable fibrin is a soft, elastic mass, dissolving in very weak acids, and alkalis, from which it is precipitated by salts.

Gliadin or *Vegetable Glue* is an adhesive substance, which dries up to a horny, translucent mass, resembling glue. It is insoluble in water, but dissolves in alcohol, acetic acid and dilute alkalis.

Hæmaglobin forms the principal part of the red blood-globules. It is soluble in water; when alcohol is added to this solution, and the liquid is left to stand at a temperature below 0°, hæmaglobin separates out in the crystalline state, the form of the crystals varying with the animals. After being dried over sulphuric acid at a temperature not above 0°, it forms a brick-red powder.

Hæmaglobin combines with many gases, forming peculiar unstable compounds. Thus it absorbs oxygen, and assumes a bright-red colour (arterial blood). When carbon monoxide is passed through this solution the oxygen is given off, and the hæmaglobin combines with the carbon monoxide, which again may be replaced by nitrogen dioxide. It also combines with acetylene and hydrochloric acid.

Arterial blood, or a solution, hæmaglobin saturated with oxygen gives an absorption spectrum containing two dark bands (Fig. 15, No. 1), which, on saturating the liquid with carbon dioxide (venous blood), are replaced by a single band as seen in No. 2. On shaking venous blood with air the two original bands make their appearance again.

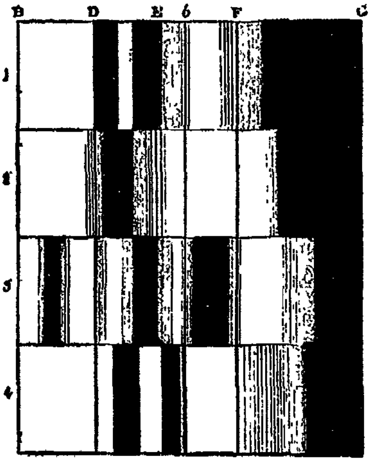


Fig. 15.

Hæmaglobin contains in 100 parts:—

Carbon	54·2
Hydrogen	7·2
Nitrogen	16·0
Oxygen	21·5
Sulphur	0·7
Iron	0·4
	100·0

Hæmatin $C_{34}H_{36}N_4O_5Fe$ is produced, together with a proteid, when hæmaglobin is treated with acids or alkalis. It is an amorphous bluish-black mass, having a metallic lustre, and dissolving in alkalis, but not in alcohol and water. It is also capable of yielding two absorption-spectra by the action of oxygen and carbon dioxide; these bands are seen in Fig. 15, Nos. 3 and 4.

Its alkaline solution may be boiled without being changed. Sulphuric acid dissolves hæmatin, and on adding water, the compound $C_{34}H_{36}N_4O_6$ is precipitated; it is an amorphous mass resembling hæmatin.

Hæmatin Hydrochloride or *Hæmine* $(C_{34}H_{36}N_4O_5Fe)_2(HCl)_3$ is produced by heating hæmaglobin with glacial acetic acid, and common salt. It crystallizes in thin rhombic plates, possessing a brownish-red colour, and bluish-red reflection. Alkalis decompose it into hæmatin and hydrochloric acid.

The formation of these *blood-crystals* is made use of as a test for detecting blood-spots in criminal cases.

Mucin is contained in the secretions of the mucous membranes and is conveniently prepared by precipitating filtered ox-bile with alcohol, dissolving the precipitate in water, and precipitating again with acetic acid. It swells up in a little water, and dissolves in a large quantity; its solution does not coagulate on heating. Mucin contains: carbon 52·2, hydrogen 7·0, nitrogen 12·6, oxygen 28·2.

Keratrin.—This name is given to the residual mass, which is obtained by exhausting epidermis, nails, claws, hoofs, hair, wool, whale-bone, &c., with ether, alcohol and a dilute acid. It dissolves in potash with the formation of ammonia and potassium sulphide, and acids produce in this solution a gelatinous precipitate. When the substances above mentioned are boiled with dilute sulphuric acid, they yield tyrosine and leucine, and nitric acid imparts to them a yellow colour. The composition of keratrin does not differ much from that of the proteids, but it contains more sulphur:—

	Percentage of Sulphur.
Human-hair	4—5
Human-nails	2·8
Epidermis	0·7
Wool	2—3·5
Horse-hoofs	4·2
Whale-bone	3·5
Tortoise-shell	2·0

Elastin is a substance resembling keratrin, and is contained in the *ligamentum nuchae* of cattle. It is in the moist state extensible, but becomes brittle after drying. Its alkaline solution is not precipitated by acids. A similar substance has been found in the egg of the common snake.

GELATIN AND CHONDRIN.

These two compounds do not pre-exist in the animal organism, but are produced by the action of boiling water on certain tissues.

Gelatin is obtained by boiling bones, tendons, skin, bladder, &c.,

with water. The pure compound, as seen in isinglass, is a colourless, glassy, brittle mass, while glue is more or less coloured. It softens in cold water, and is converted into a gelatinous mass, and with boiling water it forms a thick, viscid solution which, on cooling again, solidifies to a jelly. When a little nitric acid is added to a hot solution of gelatine it remains liquid in the cold.

Its solution is precipitated by tannin, even if very dilute, a white curdy mass separating out. The tissues yielding gelatine also combine with tannin; thus, on placing a piece of bladder or skin into a solution of tannin, the latter is completely removed and leather is formed.

When gelatin is submitted to dry distillation it yields ammonium carbonate, ammonium sulphide, ammonium cyanide, amines, pyridine bases, pyrrol, and other compounds, and when it is boiled with dilute sulphuric acid it yields, among other products, glycocoll and leucine.

The composition of gelatin is:—

Carbon	49·3
Hydrogen	6·6
Nitrogen	18·3
Oxygen	25·8
	100·0

It also contains invariably a small quantity of sulphur.

Chondrin is produced by the action of boiling water on the young bones, whilst yet in a soft state, and on the cartilage of the ribs and joints. It resembles gelatine, but differs from it by being precipitated from its solution by the addition of a little acid, and re-dissolving by adding more. When it is boiled with hydrochloric acid, it yields a fermentable sugar. Its composition is:—

Carbon	50·0
Hydrogen	6·6
Nitrogen	14·4
Oxygen	29·0
	100·0

SILK.

When raw silk is heated with water under pressure, it yields two compounds.

Fibroïn $C_{15}H_{23}N_5O_6$ constitutes about 66 per cent. of raw silk; it is a silky, glistening substance which is insoluble in water, but dissolves in strong acids, alkalis and a solution of cuprammonium sulphate. When boiled with dilute sulphuric acid it yields glycocoll, leucine and tyrosine.

By treating sponge with ether, alcohol, hydrochloric acid, and dilute soda, *spongin* is left behind, which has great resemblance to fibroïn, and also yields glycocol, and leucine, but no tyrosine.

Sericin or *Silk-gelatin* $C_{15}H_{25}N_5O_8$ is a substance resembling gelatin. Its hot aqueous solution is precipitated by alcohol, and after drying the precipitate forms a colourless powder, which in cold water swells up to a gelatinous mass. On boiling it with a dilute sulphuric acid it yields a small quantity of leucine, and larger quantities of tyrosine, and serine, or amidoglyceric acid.

FERMENTS.

Under the head of fermentation it has already been mentioned that several kinds of sugar, and other bodies such as glucosides, if a *ferment* be added to their dilute solution, are resolved into two or more new compounds. Ferments are proteids in a peculiar state of decomposition. Their constitution is quite unknown, and none of them has been yet obtained in a pure state.

Yeast consists of one of the lowest members of the vegetable kingdom (*Torula cerevisiæ*). On treating it with dilute potash the cells are disintegrated, and their contents dissolve in the potash. On adding acetic acid, white flakes are precipitated, which, after drying form a yellow, brittle mass, and contain :—

Carbon	55·0
Hydrogen	7·5
Nitrogen	14·0
Oxygen	23·0
Sulphur	0·5
	100·0

Yeast has not only the property of resolving glucose into alcohol and carbon dioxide, but also to decompose calcium malate into calcium carbonate, acetate and succinate, and to convert salicin in presence of chalc, into lactic acid, and saligenin.

When yeast is kept under water, fermentation sets in, carbon dioxide is evolved, and the liquid contains after some time a little alcohol, a kind of albumin and leucine.

By washing yeast with water, an organic substance goes gradually in solution, possessing in the highest degree the property of converting cane-sugar into inverted sugar.

Diastase.—When grain germinates a portion of one of the proteids is transformed into diastase, which may be obtained by precipitating a cold infusion of malt with alcohol in white flakes. Its aqueous solution is not coagulated on heating, and possesses the properties of converting starch into dextrin and dextrose, one part being sufficient for the conversion of 100,000 parts of starch. The composition of diastase is not known.

Emulsin or *Synaptase* is the specific ferment of bitter almonds, and exists also in sweet almonds, from which it is obtained by exhausting the powdered paste, from which the oil has been expressed with cold water, adding acetic acid to the solution to remove proteids, and precipitating the emulsin with alcohol. It is a white, friable mass, containing about 30 per cent. of calcium phosphate, and consisting, after deducting the ash, of:—

Carbon	42·9
Hydrogen	7·1
Nitrogen	11·5
Oxygen	37·3
Sulphur	1·2
	100·0

Emulsin has the specific property of decomposing amygdalin, salicin, arbutin, æsculin, and other glucosides.

Myrosin is contained in black mustard-seed, and is a substance resembling diastase. It is without any action on amygdalin, but readily decomposes potassium myronate, into mustard-oil, sugar, and acid potassium sulphate.

Pepsin is a substance resembling mucin, and is found in the gastric juice. It possesses the specific property to convert proteids in the presence of an acid, into soluble modifications, called *peptones*.

Ptyalin exists together with mucin and salts in saliva; it is sparingly soluble in water, and insoluble in alcohol, and possesses the property of changing starch into dextrin and dextrose, and decomposing salicin into sugar and saligenin.

Similar substances exist in the pancreatic and intestinal fluids, which have an alkaline reaction. The pancreatic fluid converts starch rapidly into dextrose, and proteids into peptones, and resolves fats into glycerin and fatty acids. The intestinal fluid also transforms proteids into soluble modifications, and starch into sugar, and the latter into lactic acid, and butyric acid.

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